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KINEMATIC MODELING OF MULTIPHASE SOLUTE TRANSPORT IN THE VADOSE ZONE

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16. ABSTRACT

The goal of this research was the development of a computationally efficient simulation model for multiphase flow of organic hazardous waste constituents in the shallow soil environment. Such a model is appropriate for investigation of fate and transport of organic chemicals introduced to the soil through spills on the ground surface, leakage from surface impoundments or underground storage tanks, or land treatment of hazardous wastes. During the initial phases of a site investigation there usually does not exist sufficient data to support the application of comprehensive, computationally expensive numerical models. Simplified physically based models which can address the transport of an organic constituent experiencing volatilization, multiphase partitioning, biodegradation, and migration may be preferred. Two models based on the kinematic theory of multiphase flow are developed and presented herein, along with a number of illustrative examples. The Kinematic Oily Pollutant Transport (KOPT) model assumes steady infiltration of water based on the expected annual infiltration rate; the Kinematic Rainfal and Oily Pollutant Transport (KROPT) model includes transient hydrologic phenomena (evaporation and infiltration) along with a model for stochastic generation of rainfall. The examples presented suggest that the KOPT model may be preferred for most applications.

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FOREWORD

EPA is charged by Congress to protect the Nation's land, air and water systems. Under a mandate of national environmental laws focused on air and water quality, solid waste management and the control of toxic substances, pesticides, noise and radiation, the Agency strives to formulate and implement actions which lead to a compatible balance between human activities and the ability of natural systems to support and nurture life.

The Robert S. Kerr Environmental Research Laboratory is the Agency's center of expertise for investigation of the soil and subsurface environment. Personnel at the Laboratory are responsible for management of research programs to: (a) determine the fate, transport and transformation rates of pollutants in the soil, the unsaturated and the saturated zones of the subsurface environment; (b) define the processes to be used in characterizing the soil and subsurface environment as a receptor of pollutants; (c) develop techniques for predicting the effect of pollutants on ground water, soil, and indigenous organisms; and (d) define and demonstrate the applicability and limitations of using natural processes, indigenous to the soil and subsurface environment, for the protection of this resource.

The behavior of organic hazardous waste constituents that enter the soil environment may be predicted using vadose zone transport and fate models. Such models normally consider only the presence of water, air and solid phases of the natural media. An oil phase often exists, however, which may greatly influence the fate and transport characteristics of the hazardous waste constituents. This report presents two simplified models which account for fate and transport based on multiphase partitioning between the air, wastes, oil and solid phases of the waste-soil matrix. This information should prove useful to those interested in predicting the potential fate and transport of hazardous constituents in complex vadose zone environments containing an oil phase.

Clinton W. Hall

Clinton W. Hall, Director
Robert S. Kerr Environmental
Research Laboratory

ABSTRACT

The goal of this research was the development of a computationally efficient simulation model for multiphase flow of organic hazardous waste constituents in the shallow soil environment. Such a model is appropriate for investigation of fate and transport of organic chemicals introduced to the soil through spills on the ground surface, leakage from surface impoundments or underground storage tanks, or land treatment of hazardous wastes. During the initial phases of a site investigation there usually does not exist sufficient data to warrant the application of comprehensive though computationally expensive numerical models, and simplified physically based models which can address the transport of an organic constituent experiencing volatilization, multiphase partitioning, biodegradation, and migration may be preferred. Two models based on the kinematic theory of multiphase flow are developed and presented herein, along with a number of illustrative examples. The Kinematic Oily Pollutant Transport (KOPT) model assumes steady infiltration of water based on the expected annual infiltration rate, while the Kinematic Rainfall and Oily Pollutant Transport (KROPT) model includes transient hydrologic phenomena (evaporation and infiltration) along with a model for stochastic generation of rainfall. The examples presented suggest that the KOPT model may be preferred for most applications.

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SECTION 1

INTRODUCTION

The focus of this research has been on the fate and transport of organic hazardous waste constituents in the shallow soil environment. Organic hazardous waste constituents may be introduced into the soil by spills on the ground surface, leakage from surface impoundments or underground storage tanks, or land treatment of hazardous wastes. Oftentimes in these circumstances, an "oil" phase is present in addition to the water, air, and soil of the natural media, and the fate and transport characteristics are determined by the mobility of the water and oil, as well as by multiphase partitioning of the constituent between the air, water, oil and soil matrix. The emphasis of the research has been on development of simplified models for fate and transport of organic contaminants which may be appropriate for the initial screening or investigation of a site when the available data base does not warrant the application of more general models.

The primary objectives of this cooperative agreement have been to support RSKERL in their modeling studies of subsurface contamination from organic wastes, including hazardous waste land treatment operations, and to investigate the application of kinematic models for multiphase processes including the flow of water and oil, as well as multiphase-partitioning, volatilization, and biodegradation.

The Kinematic Oily Pollutant Transport (KOPT) and Kinematic Rainfall and Oily Pollutant Transport (KROPT) programs are implementations of a kinematic multiphase transport model that was developed as a part of this research. The KOPT program is a simplified implementation of the kinematic multiphase transport model, intended to be used as a screening tool for hydrocarbon spills or near-surface releases. It addresses the questions of how far an oil release might go into the soil and how soon it might get there. In the KOPT implementation, steady water infiltration is assumed to occur, and the specified water saturation is taken as representative of climatic conditions. The KROPT program is the full implementation of the kinematic multiphase transport model and includes modeling of transient hydrologic phenomena (evaporation and infiltration), along with a model for the stochastic generation of rainfall. This model handles multiple loadings or releases of oily wastes at or near the ground surface, multiple rainfall events, potential oil migration, sorption, volatilization, and biodegradation.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

The results of this research found that kinematic theory was successfully applied to multiphase flow of water and oil. Kinematic models have an advantage over traditional numeric models in that the kinematic models are well-suited for studying the hyperbolic or wave behavior of the multiphase flow equations. Inclusion of sharp fronts is natural to the kinematic models, while finite difference or finite element models encounter difficulties when derivatives in the governing equations tend to become undefined. The kinematic model simplifies the governing equations revealing some of the fundamental behavior of the solution and showing how the oil and water fronts interact. Solution of the kinematic model indicates that the incoming water must displace all of the mobile oil for mass to be conserved. Another important result is that oil banks are formed when the incoming water displaces the oil that is present. The main limitation to the kinematic model is that displacement of oil by water may be unstable depending on the fluid properties of the oil and the speed of the incoming water.

The two computer codes written to implement two versions of the kinematic model, KOPT and KROPT, run in a computationally efficient manner, and may be used to estimate the vertical migration of oil and a dissolved constituent within the soil profile, including the effects of volatilization and biodegradation. Running these codes showed that the amount of residual oil saturation strongly affects the total depth over which the the oil will be predicted to spread.

In light of the success of kinematic models for multiphase flow problems, further development of the KOPT and KROPT programs. Specifically, the following recommendations are suggested:

- Generalize KOPT and KROPT models for use in simulation of facilitated transport. Such an application could look at the use of solvents (such as heptane) for flushing a soil profile to remove low mobility organic hazardous wastes, and then model the much more rapid volatilization and degradation of the solvent.

- Development and implementation of user-friendly versions of the KOPT and KROPT programs.

- Expand KROPT program to handle unstable displacements of oil by water, thereby eliminating the main limitation of the model and enabling the use of randomly generated rainfalls that may exceed the kinematic rate. This program enhancement would also handle cases where oil is the displacing fluid, instead of water, such as when the oil loading rate exceeds the kinematic capacity of an initially nonuniform water profile.

- Expand KROPT to handle layered systems, where the effects of the fluids crossing into media of differing intrinsic permeabilities and pore size distributions can have an important effect on their migration.

- Modify KROPT to have the option to use other oil relative permeability models, instead of the Brooks-Corey approach, such as proposed by Parker et al. (1987) and/or Stone (1970 and 1973).

- Modify KROPT to handle depth and time variability in oil residual saturations.

SECTION 3

RESEARCH BACKGROUND AND SCOPE

The objective of this research was to apply kinematic modeling theory to fate and transport of hydrocarbons in the vadose zone for oil spills and land treatment sites. The purpose of the work was to provide a way to estimate the gross movement of pollutants in a multiphase system resulting from spills, leaks and at land treatment sites. In the case of land treatment systems the long term behavior of the site is of interest, so computationally efficient simulations are needed. This was the reason for using a simplified approach.

When placed in porous media, immiscible pollutants retain their unique properties. Although these pollutants are largely immiscible in water, they are capable of causing groundwater contamination by their dissolved constituents. Immiscibility leads to distinct bodies of pollutant in close contact with both air and water, where present. Above the water table, the addition of an immiscible pollutant causes the original two-phase water/air system to become a three-phase water/pollutant/air system. When flowing, the transport and fate of immiscible fluids are governed by a set of relationships which are, basically, expanded forms of the single phase governing equations. The former provides the theoretical framework for solving immiscible (or multiphase) flow problems in general. The specific application of the theory depends on the initial and boundary conditions imposed during pollutant migration as well as other features unique to pollution incidents (Weaver, 1984).

MULTIPHASE FLOW MODELS

Currently available analytic and semi-analytic multiphase flow models share the limitation that they rely on an assumed shape of the oil profile that is not based upon solution of the governing physically based equations (Dracos, 1978, Mull, 1970 and 1978, and Raisbeck and Mohtadi, 1974). After an oil release ends, the oil is gradually replaced by air as it drains. A drainage profile, similar to those observed for water is expected, since the same forces that act on the water also act on the oil. Other phenomena outside the scope of these models are biodegradation which also causes variable oil saturations, and simultaneous unsteady flow of the water. The latter is typical of actual time-varying conditions in the field.

Only a few numeric solutions of the multiphase flow equations have been presented for the specific problem of shallow aquifer contamination (Abriola and Pinder, 1985a and 1985b, Corapcioglu and Baehr, 1987, Faust, 1985, Kuppusamy et al., 1987, Hochmuth and Sunada, 1985, and Osbourne and Sykes, 1986). A limitation of the numeric approach is that the models are computationally very intensive. To exploit fully their capacity for modeling geologic variability, a large amount of data is required. Because data is usually sparse, the full capacity of a numeric model may never be reached when applied to specific site investigations.

KINEMATIC THEORY APPLIED TO MULTIPHASE FLOW

The analytic and semi-analytic flow models illustrate that if a constant amount of water is present in the pore space, only the mass conservation equation for the oil needs to be solved. A solution, that has not been used for this purpose, is the kinematic model for soil moisture transport (Sisson et al., 1981, Smith, 1983, and Charbeneau, 1984). In addition to a solution for the duration of water application, this model gives a solution for the unsteady flow occurring in soils undergoing drainage (replacement of soil moisture by air). The solution is obtained by solving an approximate governing equation for the water by the method of characteristics (MOC). With the proper constitutive relationships for two-phase flow, the water solution is analytic. Adapting this solution for the oil phase gives a more realistic model than the analytic and semi-analytic models mentioned above, since the oil drainage profile is determined by solution of the governing equation. An analytic solution is not possible for the oil because the relative permeability function is too complicated and depends on the amount of water in the pore space. However, a semi-analytic solution for the oil phase can be achieved, allowing relatively low computation times to be achieved.

The following assumptions are used for the model formation. The model equations are solved for one-dimensional flow. This is one of the necessary assumptions to extend kinematic theory to multiphase flow. Lateral migration, however, reduces the amount of pollutants and water that move downward. The one-dimensional formulation is conservative as it will determine the maximum amount of substances that will reach a given depth. A two-component pollutant is assumed. The oil acts as an inert carrier for the dissolved pollutant. Various transformations, other than biodegradation, that the oil can undergo are not modeled. Advective transport is used to model the transport of the constituent by oil and water. Equilibrium, linear partitioning relationships are used for sorption, dissolution into the water and for volatilization into the air phase. Volatilization is modeled by applying the wet zone/dry zone model of Thibodeaux and Wang (1982) as modified by Short (1986). To extend kinematic modeling to the oil phase three more assumptions are used. First the flow of the air does not impede the flow of the liquids. Second the liquid phase transport is dominated by gravity. Lastly, the medium is assumed to be strongly wetted so that the fluid saturation distributions maintain the size ordering shown in Figure 2. These assumptions are discussed in Sections 4 and 5 below.

Under the conditions to be discussed, the kinematic model can be applied 1) to the unsteady flow of both the oil and the water and 2) to the fate and transport of the dissolved constituent. If only the advective motion of the constituent is modeled, the resulting equations are compatible with the numerical approach taken for the oil equations.

Two separate implementations were created. The first (KOPT) was of a kinematic model for the oil migration only, with a constant amount of water present in the pore space. This model is analogous to the simplified analytic and semi-analytic flow models noted above, but with the capability to simulate degrading oil and the transport of the dissolved constituent. In related research this model was coupled with a model of oil spread along the water table, which in turn supplies input for a model of solute transport in the saturated zone. Here the overall model was intended as a screening tool for oil spills. A Users Guide for the KOPT model is presented in Appendix A while the listing of the code is presented in Appendix B.

The second implementation (KROPT) was a model to investigate the interactions between incoming rainfall and oil moving within the profile. This model is suited for studying the effect of a series of rainfall events, and irrigations and cultivations on a land treatment site. There are practical limitations to application of the KROPT model and it is considered a research code at this time.

SECTION 4

MULTIPHASE FLOW PRINCIPLES FOR POROUS MEDIA

The equations that govern multiphase flow in porous media are coupled, nonlinear, partial differential equations (PDEs). There is a mass conservation equation for each fluid and for each dissolved constituent in the system. There are also auxiliary relationships which incorporate various physical phenomena into the PDEs. By nature, these latter relations are empirical, since the phenomena are highly complex and thus are not suited to exact mathematical expression. Taken together these equations form a mathematical model of the flow and associated solute transport (e.g., Peaceman, 1977, pp. 24-27).

A typical mass conservation equation may be written in one dimension as

$$\frac{\partial m}{\partial t} + \frac{\partial J_m}{\partial z} = \beta_m \tag{1}$$

where m is the mass per bulk volume of porous media, J_m is the mass flux, and β_m is the source strength. Throughout the rest of this work, the liquids will be assumed incompressible and the medium non-deformable. The resulting continuity (or phase conservation) equation is

$$\eta \frac{\partial S_i}{\partial t} + \frac{\partial q_i}{\partial z} = \beta_i \tag{2}$$

where q_i is the volume flux of fluid i, S_i is percent of the pore space filled by fluid i, and η is the porosity of the soil. S_i is the called the degree of saturation of fluid i, or more commonly, simply the saturation. In a multiphase flow system,

$$\Sigma S_i = 1 \tag{3}$$

where i represents each fluid present. In order to model the liquids with the phase conservation equations 2, the concentration of the dissolved constituent is assumed to have no effect upon the fluid's migration. Fluids for which partitioning phenomena can significantly alter the saturation during the period of simulation are not suited to this approach. Examples are the volatilization of benzene or dissolution of perchloroethene (PCE) into water.

The flux term of equation 2 can be related to fundamental properties of the system by the usage of Darcy type equations. Specifically,

$$q_i = \frac{k\, k_{ri}(S)}{\mu_i} \left(\rho_i\, g - \frac{\partial P_i}{\partial z} \right) \tag{4}$$

where z is directed positive downward, k is the intrinsic permeability of the media, k_{ri} is the relative permeability of the media to fluid i, μ_i is the dynamic viscosity, ρ_i the density, g is the acceleration due to gravity, P_i is the fluid pressure, and S stands for the set of fluid saturations. The quantity $K_{ei}(S)$ is called the effective hydraulic conductivity of the media to fluid i and is defined by

$$K_{ei}(S) = \frac{k\, k_{ri}(S)\, \rho_i\, g}{\mu_i} = K_{si}\, k_{ri}(S) \tag{5}$$

where K_{si} is the fully saturated hydraulic conductivity to i. This definition underscores that the intrinsic permeability, density and viscosity play an important role in determining the flux rates in multiphase flow systems.

Equation 4 is an extended form of Darcy's Law. It incorporates the physical phenomena occurring in a porous medium containing immiscible fluids into a form that can be used in the continuity equations. Knowledge of the geometry of each individual pore and of the fluid interactions within the matrix is not needed. This information is contained in an integrated sense in the relative permeability and capillary pressure functions. The dependence of these functions on the other fluids results in the coupling of the conservation equations.

In multiphase systems the fluid pressures are related by the capillary pressure, P_c. This fundamental relationship is defined for each pair of fluids present by

$$P_c = P_{nw} - P_w \qquad (6)$$

where the pressure, P_w, is the pressure in the wetting phase - the fluid most strongly attracted to the solid. P_{nw} is the pressure in the nonwetting fluid. For simple geometries (i.e., single circular tubes), there are analytic expressions for the capillary pressure (see e.g., Bear, 1972, pg. 446). Soils, however, are composed of a variety of irregular, tortuous pores. The relationship expressed by equation 6 still holds, but must be expanded to represent the variation in P_c which can occur over a representative elementary volume. In contrast to uniform geometries, different sized pores are filled by different fluids, and their contributions to the overall pressure difference varies.

Numerous characteristics of both the capillary pressure and relative permeability functions can be related to the underlying physical phenomena (see Weaver, 1984, pp. 57-60, 62-76). Interpretation of directly measured capillary curves reveals information concerning these phenomena. Notably, capillary pressure (and relative permeability) are subject to hysteresis. That is, the capillary pressure depends on the displacement direction, being higher during drainage (displacement of a wetting fluid by a nonwetting fluid) than during imbibition (the opposite displacement).

The relative permeability function, $k_{ri}(S)$ is the fraction of the fully saturated hydraulic conductivity existing for the set of saturations S. Numerically it is a number from 0 to 1. It quantifies the notion that the presence of other fluids reduces the hydraulic conductivity of the medium to a given fluid. Physically, this occurs due to reduction in the numbers of pores available to the fluid and due to the increased tortuousity of those remaining. These effects are illustrated by the typical two phase relative permeability curves in Figure 1. The permeabilities drop off rapidly in a characteristic manner when the saturation is reduced. At the trapped or residual saturations S_{ir}, the relative permeability is zero, implying that the fluid is not present as a continuous phase. For wetting fluids this is as fluid held in the smallest pores, while residual nonwetting fluids are found in larger pores as isolated droplets.

Due to the considerable difficulties of measurement, three-phase relative permeability is rarely measured (see Stone, 1970). Alternatively, various models of relative permeability are used. One way to develop these is to begin with conceptual

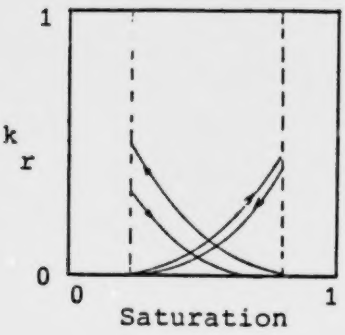

Figure 1: Typical Two-Phase Relative Permeability Curves

models of the porous medium, presumed distributions of fluids within the medium, and a solution of laminar flow through the medium (see Bear, 1972, pg. 463). The Burdine (Burdine, 1953, Wyllie and Gardner, 1958) equations form one such model. For each phase in the system there is a relative permeability equation:

$$k_{rw} = \left(\frac{S_w - S_{wr}}{1 - S_{wr}}\right)^2 \frac{\int_0^{S_w} \frac{dS}{P_c^2}}{\int_0^1 \frac{dS}{P_c^2}} \tag{7}$$

$$k_{ro} = \left(\frac{S_o - S_{or}}{1 - S_{or}}\right)^2 \frac{\int_{S_w}^{S_o+S_w} \frac{dS}{P_c^2}}{\int_0^1 \frac{dS}{P_c^2}} \tag{8}$$

Originally, the three-phase integration of the Burdine equations contained no provision for a residual oil saturation (Wyllie and Gardner, 1958). Equations 7 and 8 have been modified to fit the requirements of the definition of relative permeability: that k_{ro} equals one only when the pore space is completely filled with oil and that k_{ro} equals zero when the oil is at its residual saturation. The modification is to the squared term of equation 8, which represents the ratio of the tortuosities at full saturation to that at any saturation, S_o (Brooks and Corey, 1964). At $S_o = S_{or}$ the tortuosity is infinite, since the oil is found as disconnected blobs in the pore space. This condition gives zero relative permeability. When the oil fills the pore space (meaning that there is no residual water saturation), the tortuosity is equal to the saturated tortuosity.

The capillary pressure as a function of saturation is needed to evaluate the integrals in equations 7 and 8. Brooks and Corey (1964) proposed a power law model for drainage capillary pressure,

$$S_e = \left(\frac{S_w - S_{wr}}{1 - S_{wr}}\right) = \left(\frac{P_{ce}}{P_c}\right)^{\lambda} \tag{9}$$

where S_e is the effective water saturation, P_{ce} is the minimum capillary pressure required to force a non-wetting fluid into a fully saturated medium (the bubbling pressure), and λ is indicative of the pore size distribution. Using equation 9 in equations 7 and 8 results in the following model of drainage relative permeability for water and oil:

$$k_{rw} = \left(\frac{S_w - S_{wr}}{1 - S_{wr}}\right)^{\varepsilon} \tag{10}$$

$$k_{ro} = \left(\frac{S_o - S_{or}}{1 - S_{or}}\right)^2 \left(\left(\frac{S_o + S_w - S_{wr}}{1 - S_{wr}}\right)^{\varepsilon - 2} - \left(\frac{S_w - S_{wr}}{1 - S_{wr}}\right)^{\varepsilon - 2}\right) \tag{11}$$

where $\varepsilon = \frac{2+3\lambda}{\lambda}$. Despite its apparent analytic nature, certain parameters must always be measured to fit the model to a specific situation. For equations 10 and 11 these are the residual water and oil saturations, and the Brooks and Corey exponent. The values of S_{wr}, λ, and P_{ce} are obtainable through a procedure outlined by Brooks and Corey (1964). They are essentially the result of a capillary pressure curve measurement. An extensive tabulation of these parameters for many different soil types has been developed, making this an attractive model to use (Brakensiek et al., 1981, and Rawls et al., 1983). The value of the residual oil saturation is more difficult to obtain as less work has been done on it. Parker and Lenhard (1987) have recently published methods for estimating residual oil and air saturations. In the present work, however, a constant value of S_{or} is assumed.

Equation 10 is the same as would result from a two-phase integration of the Burdine equations. This is because in a strongly wetted system the strongest wetting phase (say water) is most strongly attracted to the solid. The most nonwetting fluid (air) is repelled. Water, then, is found in the smallest pores and grain contacts; air in the largest pores. Figure 2 illustrates this fluid distribution, and how oil acts as an intermediate phase. Visual studies confirm this distribution for some systems (see e.g., Schwille, 1988).

Figure 3 shows oil relative permeabilities from equation 11. As required, the relative permeability at the residual saturation, S_{or}, is zero. This can be verified by substituting S_{or} into equation 11. At the other endpoint, $1 - S_{wr} - S_{or}$, the hydraulic conductivity is somewhat less than one. This is also a required end point condition, because by definition, $k_{ro} = 1$ only when the pore space is completely filled with oil (see equation 5). Figure 3 resembles measured curves presented by Leverett and Lewis (1941).

Between the endpoints, the relative permeability at a given oil saturation increases with increasing water saturation. This is due to the fluid distribution illustrated in Figure 2. If the water saturation increases from that shown in Figure 2a to that in 2b, the oil is forced into larger pores. The larger pores have a lower surface area to volume ratio, which results in less resistance to flow and greater relative permeability. In the model equation this behavior is simulated by the limits of the integral in equations 7 and 8 being based on the fluid distribution.

A comparison with Stone's (1970) relative permeability model, which is based on pore blocking, showed general agreement with these values. At low water and oil

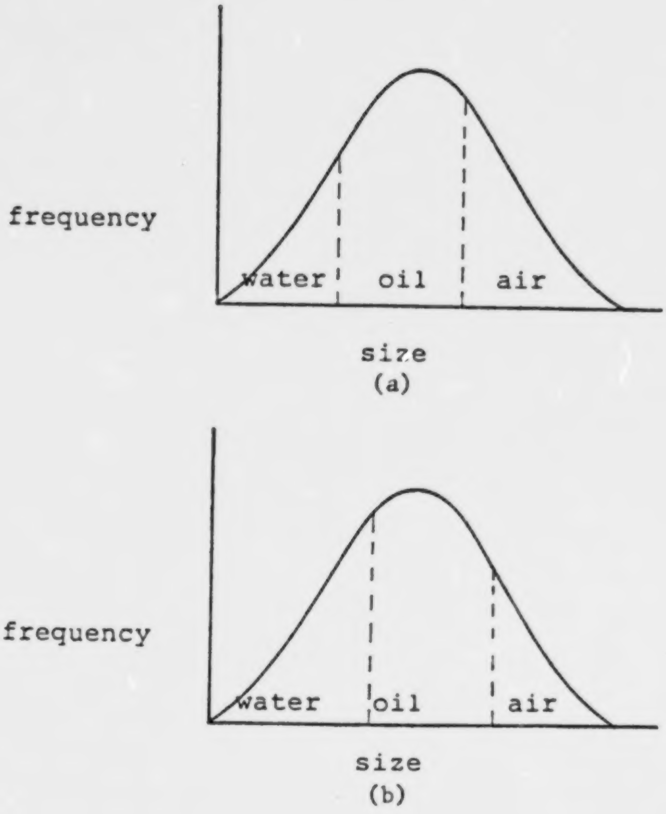
frequency
water
oil
air
size
(a)
frequency
water
oil
air
size
(b)

Figure 2: Water, Oil and Air Distribution within a Strongly Water Wet Medium; Water Saturation in (b) is greater than Water Saturation in (a)

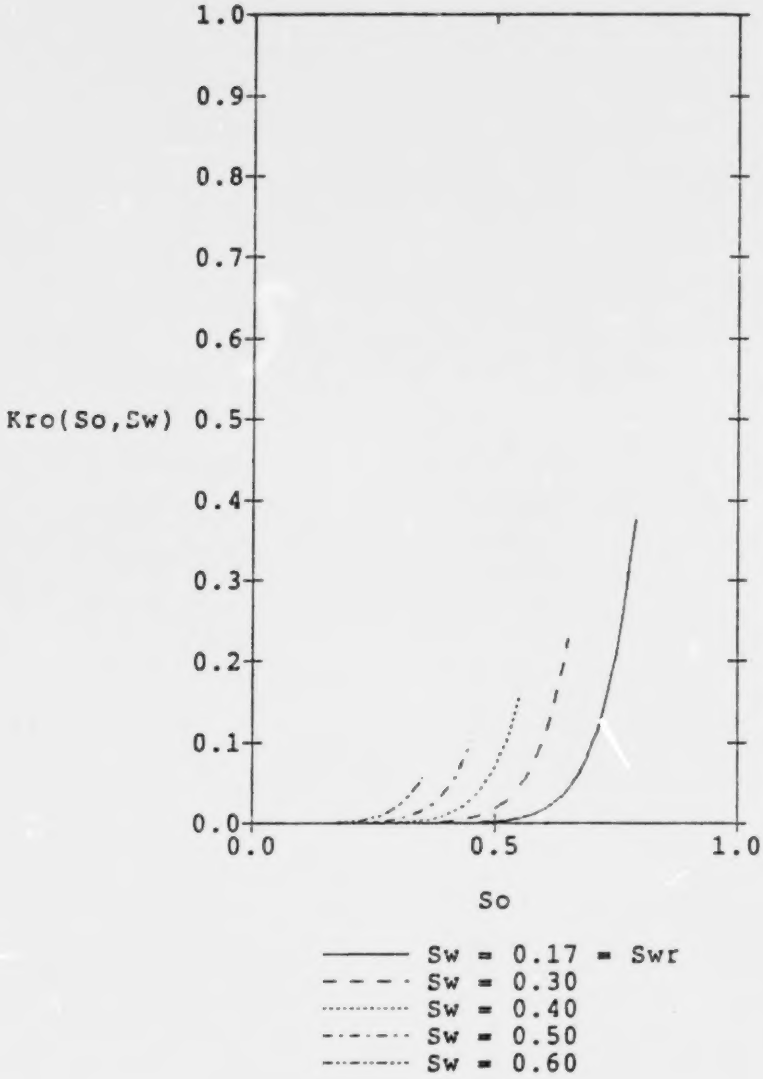

Figure 3: Oil Relative Permeability

saturations, however, increasing the water saturation reduces the oil relative permeability due to pore blocking. Throughout this region, the agreement of the models was poor, apparently because the qualitative nature of the models is different at low saturations. Both models indicate very low values of k_{ro} at these saturations. The comparison indicated that, while the Burdine equations model certain phenomena involved in oil phase permeability (relative tortousity and resistance of pores occupied), they do not necessarily include all the phemonema. In their review, Saraf and McCaffery (1981) recommended using either the Burdine equations or Stone's (1970) model. Delshad and Pope (1987) reviewed a variety of k_{ro} models with regard to available data. The latter review showed that different models fit different sets of measured relative permeability data best. This indicates that three-phase relative permeability modeling is an area that needs further development. The three-phase Burdine equations were selected for this work, since their behavior is very regular.

In most cases of interest the oil applied at the ground surface will contain dissolved constituents. These may partition between the water, oil, air, and soil phases. A mass conservation equation for these may be written by using equation 1 and appropriate expressions for the mass of the constituent per unit volume and the mass flux. The total mass of constituent per unit bulk volume, m_c, is

$$m_c = \eta\,(S_oC_o + S_w C_w + S_aC_a) + \rho_bC_s \qquad (12)$$

where η is porosity, C_o, C_w, and C_a are the constituent concentrations in oil, water, and air, ρ_b is the soil's bulk density, and C_s is the sorbed concentration expressed as mass of constituent/mass of soil. The mass flux is

$$J_c = q_oC_o + q_wC_w + q_aC_a - D_o\frac{\partial C_o}{\partial z} - D_w\frac{\partial C_w}{\partial z} - D_a\frac{\partial C_a}{\partial z} \qquad (13)$$

where D_o, D_w, and D_a are the dispersion coefficients for the constituent in the oil, water, and air phases. Using partitioning relationships of the form

$$C_j = f_j(C_w) \qquad (14)$$

where the subscript j refers to oil, air or soil, allows the constituent mass conservation equation to be written in terms of one unknown concentration, say, C_w.

SECTION 5

THE KINEMATIC MODEL

Three physically based assumptions give rise to the kinematic model. They are of central importance to the model, and will be discussed first in this section. Following the discussion of the assumptions, the derivation of the model equations and their solution will be presented.

MAJOR ASSUMPTIONS OF THE MODEL

The first assumption of the model is to follow Richards (1931) and neglect resistance to air flow in the mass conservation equation for water. This is in accordance with common soil science practice and many of the other multiphase infiltration models. Richards' assumption means that the flow of the air does not affect the flow of the liquid, and this assumption is usable as long as pressure does not build up in the air phase (Youngs and Peck, 1964). The presence of air is accounted for via the usage of a three phase relative permeability function, and by assuming that there is a residual air saturation. Experience shows that the maximum effective hydraulic conductivity to water is 40% to 60% of K_{ws} (Bouwer, 1966). For the modeling, 50% K_{ws} is used to determine the trapped air saturation. Typically this is a fairly small value (< 0.05), since the relative permeability drops off rapidly.

Second, a gravity drainage or kinematic model is used. Several comments on the kinematic assumption are warranted. The theory of kinematic waves was presented by Lighthill and Whitham (1955) for flood waves in rivers. They noted that whenever an approximate functional relation exists at each point between the flux and concentration (saturation) then the wave motion follows directly from the equation of continuity. For most cases of interest the functional relation is nonlinear, and the kinematic waves are either self-spreading, self-sharpening, or regions of constant state. For multiphase flow the self-spreading wave corresponds to a region of internal drainage and redistribution. Here, the saturation gradients decrease with time as does the role played by pressure gradients. The self-sharpening wave corresponds to a wetting front. While capillary pressure gradients determine the actual shape of a wetting front, the kinematic model is able to move the sharp-front representation of the wetting front downward at the correct speed so that mass is conserved. For these reasons, kinematic models are able to represent the essential features of nonlinear wave phenomena.

In addition to the comments concerning the ability of kinematic models to represent the important features of soil water and hydrocarbon waves, one must distinguish between the capillary pressure in individual pores and the macroscopic capillary pressures appearing in the flux equation. Two ways of representing the underlying phenomena on a macroscopic scale are with the relative permeability and capillary pressure functions. Research done in studying the effects of reducing interfacial tensions (Bardon and Longeron, 1980) shows that in the absence of interfacial tension (i.e., pore level capillary pressures), the relative permeability is equal to the saturation, otherwise k_r is less than S. Using a $k_r(S)$ function similar to that appearing in Figure 1 assures inclusion of capillary phenomena in the model. The same point is illustrated indirectly by equations 7 and 8, which model k_r as a function of the macroscopic capillary pressure function.

For a hydrocarbon release, initially, strong capillary gradients drive the flow. These are included through use of a Green and Ampt (1911) type of model for both the water and hydrocarbon phase with a corresponding wetting front suction pressure. Following the initial wetting period there is a transition period, which leads later to gravity dominated flow (Philip 1969, pg. 280). Under the kinematic assumption only the term involving the gravity force is retained explicitly in the liquid flux equations (equation 4), while the effects associated with capillary pressures are approximately handled implicitly within the model.

The third assumption for the model is that in a strongly wetted system, the relative permeability to the wetting phase is independent of the other fluids present. The reason for this is that the most wetting phase is so strongly attracted to the medium that it occupies the smallest pores no matter what other fluids are present (see Figure 2). Fayers and Matthews (1984) reviewed experimental results extensively and concluded that most researchers would agree with this assumption in strongly wetted systems. Note that most of the commonly used models of relative permeability (Burdine, Stone, Parker et al, etc.) are predicated upon the assumption of a distribution of fluids within the medium that would exist in a strongly wetted system. Consequently, relative permeability models for the strongest wetting phase are independent of the other saturations.

DERIVATION AND SOLUTION OF THE MODEL EQUATIONS

The derivation of the model proceeds from the governing equations and assumptions as follows. The water flux, q_w, is given as the gravity component of equation 4

$$q_w = K_{ew}(S_w) \tag{15}$$

Next the continuity equation for water can be written in terms of its unknown saturation, S_w, by expanding the z derivative. The resulting first order hyperbolic equation is

$$\eta \frac{\partial S_w}{\partial t} + \frac{dK_{ew}(S_w)}{dS_w} \frac{\partial S_w}{\partial z} = 0 \tag{16}$$

where its source term is zero because it is assumed for the present argument that water is conserved within the profile (later the question of water loss through evaporation will be addressed). In equation 16 all quantities are expressed in terms of kinematic variables (length and time only), hence the name kinematic model.

After application of the kinematic assumption, the oil equation can be written in terms of the unknown saturation, S_o. The resulting first order hyperbolic equation is

$$\eta \frac{\partial S_o}{\partial t} + \frac{\partial K_{eo}(S_o,S_w)}{\partial S_o} \frac{\partial S_o}{\partial z} + \frac{\partial K_{eo}(S_o,S_w)}{\partial S_w} \frac{S_w}{\partial z} = - \lambda_o S_o \eta \tag{17}$$

where the first order decay term has been used for the source term to account for the possible biodegradation of the oil since oil might not be conserved; λ_o is the decay constant. The third term on the left hand side results from the dependence of the oil relative permeability on S_w. As noted below, for both water and oil the drainage relative permeability functions are used (equations 10 and 11).

The simplified model equations (16 and 17) can be written in matrix form as

$$\frac{\partial \mathbf{S}}{\partial t} + \mathbf{A} \cdot \frac{\partial \mathbf{S}}{\partial z} = \mathbf{B} \tag{18}$$

with

$$\mathbf{S} = \begin{Bmatrix} S_w \\ S_o \end{Bmatrix}$$

$$\mathbf{A} = \frac{1}{\eta} \begin{Bmatrix} \frac{dK_{ew}}{dS_w} & 0 \\ \frac{\partial K_{eo}}{\partial S_w} & \frac{\partial K_{eo}}{\partial S_o} \end{Bmatrix}$$

$$\mathbf{B} = \begin{Bmatrix} 0 \\ -\lambda_o S_o \end{Bmatrix}$$

The system of equations is hyperbolic if the eigenvalues of the matrix **A** are real and distinct (Whitham, 1974 and Lax, 1973). The eigenvalues of **A** are easily determined as they are identical to the diagonal entries (Kreyszig, 1972, page 277) divided by η. These are always real, since they are the derivatives of the real functions k_{rw} and k_{ro} (equations 10 and 11). The values are also distinct for cases of practical interest.

The consequences of strong wetting on kinematic flow are apparent in matrix **A**. For water in a strongly water wet system, the kinematic flux (relative permeability) is independent of the other fluids. This results in the partial derivative of the water flux with respect to oil saturation S_o, being equal to zero. The mass conservation equation for the water is independent of the other equations, and can be solved first. This is true only as long as the flow remains kinematic, and the "0" element remains in matrix **A**.

Since the system of equations is hyperbolic, the method of characteristics can be used to determine the solution. Where the water saturation distribution varies continuously, the classical method of characteristics solution of equation 16 is

$$\left.\frac{dz}{dt}\right|_{S_w} = \frac{1}{\eta} \frac{dK_{ew}(S_w)}{dS_w} \tag{19}$$

Equation 19 is valid only where the derivatives appearing in equation 16 exist at each point of the solution domain (see Rozdestvenskii and Janenko, 1980). When the derivative, $\frac{dK_{ew}(S_w)}{dS_w}$, is a known function, equation 19 can be integrated analytically, leading directly to an expression of z as a function of time. Then for a given saturation and time, the associated depth is known immediately. This is the case with relative permeability equation 10 (Charbeneau, 1984).

After obtaining the solution of the water equation, equation 17 for the oil phase may also be solved by the method of characteristics. Application of the method of characteristics gives the result:

$$\frac{dS_o}{dt} = -\frac{1}{\eta}\frac{\partial K_{eo}(S_o,S_w)}{\partial S_w}\frac{\partial S_w}{\partial z} - \lambda_o S_o \qquad (20)$$

along

$$\frac{dz}{dt} = \frac{1}{\eta}\frac{\partial K_{eo}(S_o,S_w)}{\partial S_o} \qquad (21)$$

Equation 21 is the projection of the characteristic path onto the base characteristic plane (the z-t plane). In cases where S_w is constant, equation of 20 has the well-known analytic solution for exponential decay

$$S_o(t) = S_o(\tau)\exp\left[-\lambda_o\,(t-\tau)\right] \qquad (22)$$

where τ is the time origin of the characteristic. The solution, equation 20, also exists only where the saturation derivatives appearing in equation 17 exist in the solution.

The method of characteristics has been used to reduce the coupled set of first order quasi-linear partial differential equations 18 to the set of ordinary differential equations specified by equations 19, 20 and 21. The resulting ordinary differential equations are easier to solve numerically. All of the remaining parts of the solution will also be written as ordinary differential equations or, when possible, analytic solutions.

For the kinematic model the saturation derivatives may fail to exist, because smooth solutions of quasilinear hyperbolic equations do not necessarily exist throughout the whole solution. A discontinuity may develop after a finite period of time (Jeffrey and Taniuti, 1964). In this case integral equations are used to find alternative solutions that are called generalized or weak solutions. One place where this occurs is at the leading edge of a liquid infiltrating into the soil, also called a wetting front. In the absence of capillary pressure gradients, the gravity drainage model causes the derivative, $\partial S/\partial z$, to tend to infinity for the infiltrating fluid. The derivation of the generalized solution will be illustrated by the water equation.

An integral form of the continuity equation 2 applied to a control volume around the front gives

$$\int_{z_1}^{z_2} \eta \frac{\partial S_w}{\partial t} dz + \int_{z_1}^{z_2} \frac{\partial q_w}{\partial z} dz = 0 \tag{23}$$

where the integrals are evaluated from points z_1 to z_2 shown on the water profile of Figure 4. The integrals can be evaluated analytically if the true front is replaced by the sharp front shown in Figure 4. Note that the idealized profile contains the same volume of water as does the true profile. For the idealized profile,

$$\eta \frac{d}{dt}\left[\int_{z_1}^{z_f} S_w \; dz + \int_{z_f}^{z_2} S_w \; dz \right] + K_{ew}(S_{w2}) - K_{ew}(S_{w1}) = 0 \tag{24}$$

The exchange of differentiation and integration is permissible since z_1 and z_2 are fixed locations. The pressure gradient term of the flux vanishes because the integration is carried out between points where $\partial S_w/\partial z$ is zero. Completing the integration gives

$$\frac{dz_f}{dt} = \frac{K_{ew}(S_{w1}) - K_{ew}(S_{w2})}{\eta \; (S_{w1} - S_{w2})} \tag{25}$$

for the water. The similar oil equation is

$$\frac{dz_f}{dt} = \frac{K_{eo}(S_{o1},S_{w1}) - K_{eo}(S_{o2},S_{w2})}{\eta \; (S_{o1} - S_{o2})} \tag{26}$$

Equations 25 and 26 are the solution of equation 18 in the weak or integral sense. They are the well-known jump conditions (Whitham, 1974, page 138). In obtaining these results, the true fronts were approximated by sharp fronts. After the initial period, when the capillary gradients affect the infiltration rate, their primary effect is to spread the fronts. As a result some amount of the liquids will be deeper than this model predicts. At all times, however, the mean displacement speeds of the true fronts are the same as those used in the kinematic model and the model is conservative (Charbeneau,1984).

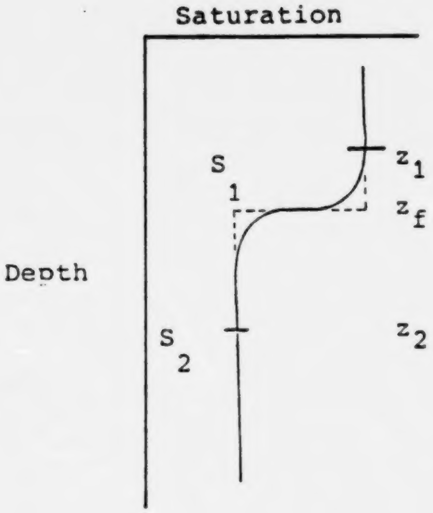

Figure 4: Profile for Generalized Solution

Taken together, the method of charactisitics solution and the jump equation 19 and 25 comprise the approximate solution for the water. Equation 19 is used where the water saturation is continuous, while equation 25 is used to determine the location of the front. Note that in the limit as S_{w1} - S_{w2} approaches zero, equation 25 becomes equation 19. Charbeneau (1984) continued by using equations 19 and 25, along with a two phase version of the Burdine-Brooks-Corey model (equation 10) to develop an analytic solution for a single water infiltration event. He also provided integral solutions for multiple rainfall events. The infiltration model of Green and Ampt (1911) with the time to ponding determined by the model of Mein and Larson (1973) are used to supplement the kinematic infiltration model (see the development in Chow, et al, 1988). In addition, the evaporation model of Charbeneau (1988) is used to modify the kinematic formulation for the water. For the oil, the method of characteristics solution and jump equation (20, 26) and the relative permeability model (eq. 11) describe kinematic unsteady oil infiltration in a strongly water wet medium, where Richards' assumption holds. Due to the relative complexity of the oil relative permeability function, no analytic solution exists for unsteady flow of oil.

THE SOLUTION FOR THE DISSOLVED CONSTITUENT

In this work the kinematic model is also applied for the dissolved constituent. This is justified in part from the fact that advection, multiphase partitioning, volatilization, and degradation are the major controls on transport and fate for many organic contaminants. Dispersion serves to spread concentration fronts and will result in an earlier arrival time at the water table. However, the kinematic model does move the concentration fronts at the correct speed for mass conservation. In addition, it is much simpler to implement, it easily includes other processes which are important, and it is much less data and computationally intensive than full dynamic models. For these reasons the kinematic model appears to be especially attractive for application during the initial phases of site investigations.

The dissolved constituent model solution proceeds as follows. For the nondiffusive migration of a constituent initially dissolved in the oil, equation 12 and the advective portion of equation 13 are substituted into the general mass conservation equation 1,

$$\frac{\partial}{\partial t}\left(\eta\, B(S_o,S_w)\, C_w\right) + \frac{\partial}{\partial z}(q_o C_o + q_w C_w) = -\, \lambda_c\, \eta\, B(S_o,S_w)\, C_w \qquad (27)$$

where $B = B(S_o,S_w) = (S_w + S_o k_o) + \rho_b k_s/\eta$ and λ_c is the constituent first-order decay constant. For consistency with the assumption that the flux of air is neglected; partitioning into the air phase is not used in the mass balance equation for the constituent. A separate model is used for volatilization, and treats volatilization as a loss from the top of the constituent profile. This will be discussed below with the volatilization model. Expanding the derivatives, while applying the linear partitioning relationships

$$k_o = \frac{C_o}{C_w}$$

$$k_s = \frac{C_s}{C_w} \tag{28}$$

$$k_w = 1$$

gives

$$\eta\, B \frac{\partial C_w}{\partial t} + \Sigma\, q_i\, k_i \frac{\partial C_w}{\partial z} + C_w\left(\frac{\partial \eta B}{\partial t} + \frac{\partial \Sigma q i\ k i}{\partial z}\right) = -\, \lambda_c\, \eta\, B\, C_w \tag{29}$$

After the saturations of water and the oil are known, C_w is the only unknown in equation 29.

Applying the continuity equations for oil and water to the third term of equation 29 gives the result that

$$\eta\, B \frac{\partial C_w}{\partial t} + \Sigma\, q_i\, k_i \frac{\partial C_w}{\partial z} + C_w\left(-\lambda_o S_o \eta k_o\right) = -\, \lambda_c\, \eta\, B\, C_w \tag{30}$$

which becomes, upon rearrangement

$$\frac{\partial C_w}{\partial t} + \frac{q_w + q_o k_o}{\eta\, B(S_o,S_w)} \frac{\partial C_w}{\partial z} = -\, \lambda_c C_w + \frac{\lambda_o S_o k_o C_w}{B(S_o,S_w)} \tag{31}$$

Applying the method of characteristics results in

$$\frac{dC_w}{dt} = C_w\left(-\, \lambda_c + \frac{\lambda_o S_o k_o}{B(S_o,S_w)}\right) \tag{32}$$

along

$$\frac{dz}{dt} = \frac{q_w + q_o k_o}{\eta\, B(S_o,S_w)} \tag{33}$$

The variables in equation 32 may be separated and integrated over a time interval from t_1 to t_2 to give

$$\ln\left[\frac{C_w(t_2)}{C_w(t_1)}\right] = -\lambda_c(t_2 - t_1) + \int_{t_1}^{t_2} \frac{\lambda_o S_o k_o}{B(S_o,S_w)}\,dt \qquad (34)$$

An analytic solution can be obtained where the water saturation is constant. The oil saturations in the third term of equation 34 vary in time according to the exponential decay relation (equation 22). For a constant water saturation and with equation 22, equation 34 becomes

$$C_w(t_2) = C_w(t_1)\exp\left\{-\lambda_c(t_2 - t_1)\right\} \frac{B(S_o(t_1),S_w)}{B(S_o(t_2),S_w)} \qquad (35)$$

This equation shows that in the absence of oil decay the constituent concentration changes in accordance with its own first order decay. When the oil decays, $B(S_o(t_1),S_w) > B(S_o(t_2),S_w)$ as there is less of the constituent dissolved in the oil, merely because there is less oil present at time t_2. All the concentrations must increase as there is less total solvent present.

When the water saturation varies, the integral in equation 34 must be evaluated numerically over the interval from t_1 to t_2. This integration must be carried out along the path that the constituent characteristic takes during the time interval. Thus the constituent concentration is given by

$$C_w(t_2) = C_w(t_1)\exp\left\{-\lambda_c(t_2 - t_1)\right\} \exp\left\{\int_{t_1}^{t_2} \frac{\lambda_o S_o k_o}{B(S_o,S_w)}\,dt\right\} \qquad (36)$$

Evaporation of water from the profile removes solvent in an analogous manner to biodegradation of the oil. Where evaporation is occurring locally from the profile, the source strength in the continuity equation 2 is equal to minus the local evaporation rate, e^*. To account for the evaporation a third multiplicative correction term is added to equation 36. This term is

$$\exp\left\{ \int_{t_1}^{t_2} \frac{e^*}{\eta\, B(S_o,S_w)}\, dt \right\} \tag{37}$$

Charbeneau's (1988) evaporation model tracks the cumulative evaporation, E, from the soil profile. The profile evaporation rate, e, is equal to $\frac{dE}{dt}$. In turn, the local evaporation rate is related to e through $e = \int e^*\, dz$, where the integral is over the depth of the uppermost soil water wave. For the kinematic model, the water saturation profile is known analytically, and one can separate the saturation change at a given depth due to drainage from that change due to evaporation. With this separation, the local evaporation rate is determined from

$$e^* = \eta \frac{\partial S_w}{\partial t} \Big|_z \text{(evaporation)} \tag{38}$$

Quantitatively, the concentration change associated with evaporation is not found to be significant, and this representation is discussed in more detail in Charbeneau, et al (1988).

For the constituent decay the analytic solution, with corrections for oil decay and water evaporation was selected in favor of solving equation 32 numerically. Indeed the inflation factors in equations 36 and 37 are evaluated numerically in the code (via the trapezoidal rule). This approach was selected, since the oil's half life is expected to be long relative to the solution step size, leading to a small correction in concentration per step. The evaporation correction was found to be very small and difficult to implement (see example 5).

Equations 35 or 36 give the concentration at time t_2, if the concentration at time t_1 is known. The concentration at the beginning of simulation is determined as follows. The constituent concentration in the released oil changes instantly upon placement in the soil because of the local equilibrium assumed for the constituent. For situations where the oil flux is specified, the constituent concentration in water in the soil can be determined by balancing mass fluxes across the surface of the soil:

$$C_{o(surface)}\, q_o = C_{w(initial)}\, (q_w + q_o\, k_o) \tag{39}$$

This relation supplies the initial concentration, $C_{w(initial)}$, for each constituent characteristic. Equation 39 shows that only if the water flux is zero will the initial concentration in waste oil be the same as that in the soil. Otherwise, $C_{o(soil)} < C_{o(surface)}$. When a specified volume of oil is applied to a zone of thickness, d_{pz}, the initial concentration is calculated via equation 12:

$$C_{o(surface)} V_o = C_{w(initial)} B(S_o, S_w) d_{pz} \tag{40}$$

where V_o is the volume of applied oil.

In the same way as integral equations apply at discontinuities in the liquid saturations, an integral conservation law applies at discontinuities (which are assumed to exist due to nondiffusive transport) in the constituent concentration. It is easy to show that for a linear governing equation, the solutions are the same for the integral and the differential forms. Equation 31 is semi-linear since the partial derivative with respect to z is multiplied by a function of z, but the result still holds. Equation 32 is the solution for both the integral and differential conservation equations. Another characteristic of linear and semi-linear equations is that the speed given by 32 is independent of the concentration.

When the dissolved constituent is volatile, emissions from the soil may contribute to atmospheric contamination. The tendency for the constituent to volatilize is related to its Henry's law coefficient, k_h. Volatilization of the constituent is modeled according to a simplified method proposed by Thibodeaux and Wang (1982). A ``dry" zone is assumed to develop in the soil that lacks any of the volatile constituent. This zone begins at the ground surface and becomes deeper as volatilization proceeds. Short (1986) modified the model by adding resistance due to diffusion through a boundary layer at the surface. The volatile flux is determined by diffusion through the soil and through the atmospheric boundary layer.

Placing a control volume on the boundary between the wet and the dry zones, as shown in Figure 5, gives the following integral mass conservation relationship

$$\int_d^w \frac{\partial m}{\partial t} dz + \int_d^w \frac{\partial J}{\partial z} dz = 0 \tag{41}$$

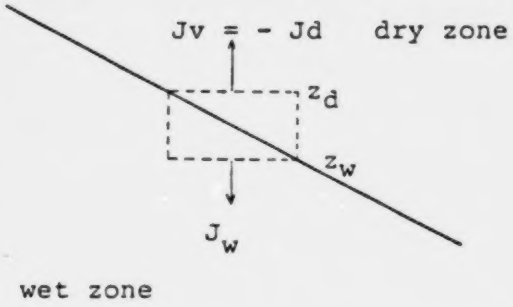

Figure 5: Control Volume for Volatilization Model

where d and w refer to the dry and wet zones, m is the mass of constituent and J is the mass flux. Applying Liebnitz rule,

$$\frac{d}{dt}\int_d^w m\,dz + m_d\frac{dz_d}{dt} - m_w\frac{dz_w}{dt} + J_w - J_d = 0 \quad . \tag{42}$$

Allowing the control volume to move with the speed of the discontinuity, such that the mass inside the control volume is constant gives

$$\frac{dz}{dt} = \frac{J_d - J_w}{m_d - m_w} \quad . \tag{43}$$

The mass in the dry zone is approximated as being zero and the flux there is the volatile flux, $-J_v$. Since the top of the zone contaminated by the constituent can move downward due to the flow of the oil and the water, J_w is equal to the constituent flux given by the advective portion of equation 13. The speed of the advancing dry zone is given by

$$\frac{dz}{dt} = \frac{J_v + (q_o k_o + q_w)C_{wd}}{B(S_o,S_w)C_{wd}} \tag{44}$$

where C_{wd} is the constituent concentration just ahead of the dry zone and the oil and water saturations are those on the boundary. Equation 44 is equal to the speed of the nonvolatile constituent (equation 32) plus the speed due to the volatilization. The additivity is due to the linearity of the governing equation. If the speed determined by equation 44 is greater than the speed of the leading edge of the dissolved constituent, then at some time the entire amount of the constituent is volatilized.

This approach uses only the diffusive flux to model the volatilization of the constituent. The volatilized constituent is assumed to rise to the surface in response to the concentration gradient. Implicitly, the vapor is taken to be of neutral buoyancy. Some vapors, however, may be denser than air and so sink into the soil. An indication of the tendency for the vapor to sink can be determined by the following. A pure chemical's vapor density relative to dry air, RVD, at 20 degrees C may be calculated from the molecular weight, MW, and the vapor pressure in torr, p_o, of the constituent by

$$RVD = \frac{\frac{p_o}{760} MW + \frac{760 - p_o}{760} 29.0}{29.0} \tag{45}$$

according to Schwille (1988). (The factor of 29.0 changes to 28.5 if air at 100% relative humidity is used instead of dry air.) The vapor pressure may be approximated from the boiling point and the heat of vaporization using the Clausius-Claperyron equation. The partial pressure resulting from the chemical in solution can then be determined by (Stumm and Morgan, 1981, pg. 728)

$$p_a = p_o \frac{C_a}{C_{sw}} \tag{46}$$

where C_{sw} is the water solubility of the constituent. Substituting the last equation into equation 45 gives the density of the vapor resulting from the constituent dissolved in water. Lower vapor densities are obtained for constituents below their aqueous solubilities, which is the anticipated condition for this modeling work.

INITIAL AND BOUNDARY CONDITIONS

Table 1 shows the boundary conditions that are applied to the model. For oil spills constant fluxes are specified for the oil, water and constituent fluxes. Initially constant concentration and saturations are specified. A generalization of the initial condition for water is discussed below in the KROPT model results discussion. For land treatment the conditions are generally similar, except that the initial concentration and saturation are specified over the depth of the plow zone, d_{pz}.

NUMERICAL TECHNIQUES

The result of the assumptions used in the above discussion is that the method of characteristics can be used for water, oil and the dissolved constituent. The original nonlinear system of coupled PDEs has been reduced to a system of nonlinear ordinary differential equations (ODEs). The weak solutions for the discontinuities and the volatilization model are also in the form of ordinary differential equations.

The solution of the model equations is obtained through the use of an ordinary differential equation solver as suggested by Greenberg (1978, pg. 569). With such a technique the solution of a system of n equations of the form

$$\frac{dz}{dt} = f_n(z_1, z_2, z_3, ..., z_n) \tag{47}$$

may be obtained, if appropriate boundary conditions are specified. The functions f_n may be coupled and/or nonlinear functions of the z_i. For the models that will be presented a Runge-Kutta-Fehlberg (RFK) method was selected. The details of this type of method was originally derived by Fehlberg (1969). A sample implementation can be found in Forsythe, Malcolm and Moler (1977).

There are several advantages to using a differential equation solver instead of finite difference or finite element techniques for this problem. Use of the differential equation solver leads to simplified programming in the sense that the programmer supplies the functions on the right hand side of equation 47 to the solver in a subroutine. No additional treatment is needed for their solution, except as detailed below. In discretization methods,

Table 1: Initial and Boundary Conditions

Boundary Conditions: Oil Spills

q_o = constant	duration of oil spill
q_c = constant	duration of oil spill
$q_o = 0$	otherwise
$q_c = 0$	otherwise
$q_v = \begin{cases}\text{constant, or}\\ \text{declining}\\ \text{amount}\end{cases}$	duration of rainfall
$q_v = 0$	otherwise

Initial Conditions: Oil Spill

$S_o = 0$	$0 \le z < \infty$
$C = 0$	$0 \le z < \infty$
S_v = constant	$0 \le z < \infty$
$S_a > S_{ar}$	$0 \le z < \infty$

Boundary Conditions: Land Treatment

$q_o = 0$	$t \ge 0$
$q_c = 0$	$t \ge 0$
$q_v = \begin{cases}\text{constant, or}\\ \text{declining}\\ \text{amount}\end{cases}$	duration of rainfall
$q_v = 0$	otherwise

Initial Conditions: Land Treatment

$S_o = S_o(0)$	$0 \le z < d_{pz}$
$C = C(0)$	$0 \le z < d_{pz}$
$S_o = 0$	$d_{pz} \le z < \infty$
$C = 0$	$d_{pz} \le z < \infty$
$S_v = S_v(0)$	$0 \le z < \infty$
$S_a > S_{ar}$	$0 \le z < \infty$

however, knowledge of specialized procedures is needed, particularly for nonlinear equations such as these.

Second, the RKF methods test for truncation error in the solution. The solver maintains the truncation error below a specified tolerance, by reducing the time step. This feature operates automatically during the program execution, resulting in a variable time step routine. The method used here, RKF1(2), uses a first order scheme to get the solution, and an embedded second order scheme to check the truncation error. This method was selected since it requires the fewest number of function evaluations of the Fehlberg methods. The trade off is that smaller time steps may be required to maintain the truncation error tolerance, since the method is of low accuracy.

Third, under certain conditions only a few of the equations need to be solved. For example, the characteristics for nondegrading oils with constant water saturation are straight lines, and only the equations for the discontinuities are solved. Much of the computational work is eliminated, since the characteristic equations have an analytic solution (i.e. a straight line).

A final advantage is that the location of the fronts is determined directly as a function of time. In a discretization method, node points must be placed on points of discontinuity. In these problems the discontinuities move with time, making it difficult to specify node point locations in advance. Further, the equations for the discontinuities are used precisely because the saturation derivatives do not exist at sharp fronts. Despite the simplification by assuming sharp fronts, in the true fronts the derivatives tend to become undefined at these locations. This presents difficulties for finite difference and finite element methods.

A departure from typical usage of RKF solvers was made for these codes. In addition to the truncation error control of the method, a fairly complicated and specialized system of ad hoc controls is needed to assure the accuracy of the solution. For example the following features of the solution must occur at times the solver picks for the solution:

- the beginning and end of rainfall and oil events,
- the end of maximum oil and water saturation regions,
- the origin of any characteristic,
- the time when water or oil fronts pass each other,

- the time when ``oil banks" are created,
- irrigation and loading times for land treatment,
- and others.

The checks are implemented in a controller routine that is called by the RKF solver. A beneficial side effect of using the controller is that the number of steps rejected for truncation error violations is reduced, since the solver is guided to critical times in the solution by the controller.

The overall structure of the program remains simple: a system of ordinary differential equations solved by the RKF solver, subject to a set of controls. A flow chart illustrating the program structure is presented in Figure 6. The method requires at most three function evaluations per time step (blocks A,B and C of Figure 6). If the solution for a time step is accepted, the third evaluation is equal to the first evaluation for the next time step. The first evaluation is only needed for starting the solver and when steps are rejected. In practice approximately 2.2 to 2.4 evaluations per step were needed on the average. If the step is acceptable in regard to both the controller and the truncation error checker, then the time step is increased and the solution proceeds. Otherwise the time step is cut and the step is retaken.

Several additional numerical techniques are used in the RKF solver for special purposes. In many cases the relationships in the model are nonlinear, necessitating the solution of single nonlinear algebraic equations. An example is the inversion of the oil relative permeability equation to determine the saturation associated with a given flux. The bisection method is used for these problems, since it is guaranteed to converge if the search interval contains the solution. The main disadvantage of the bisection method is that it is the slowest method of solving nonlinear equations (e.g. Forsythe, Malcolm and Moler, 1977, pg. 157). The secant method was tried for some of the nonlinear equations but discarded because in some cases the solutions oscillated and/or failed to converge in some cases.

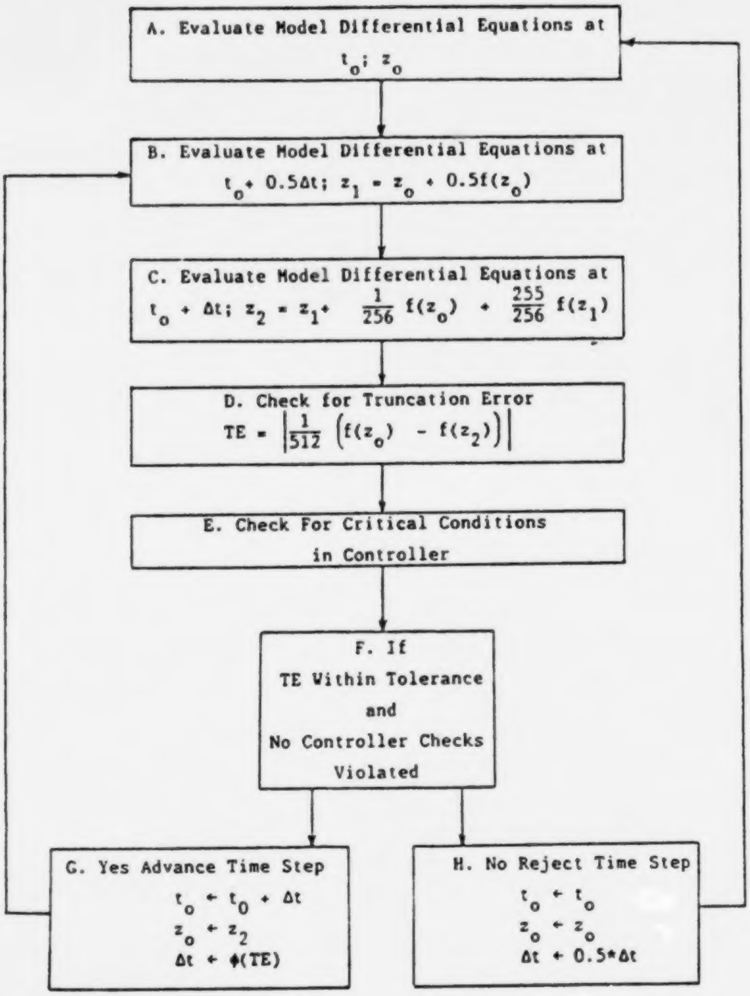
A. Evaluate Model Differential Equations at
t_o; z_o
B. Evaluate Model Differential Equations at
$t_o + 0.5\Delta t$; $z_1 = z_o + 0.5f(z_o)$
C. Evaluate Model Differential Equations at
$t_o + \Delta t$; $z_2 = z_1 + \frac{1}{256} f(z_o) + \frac{255}{256} f(z_1)$
D. Check for Truncation Error
$TE = \left|\frac{1}{512}\left(f(z_o) - f(z_2)\right)\right|$
E. Check For Critical Conditions in Controller
F. If TE Within Tolerance and No Controller Checks Violated
G. Yes Advance Time Step
$t_o \leftarrow t_0 + \Delta t$
$z_o \leftarrow z_2$
$\Delta t \leftarrow \phi(TE)$
H. No Reject Time Step
$t_o \leftarrow t_o$
$z_o \leftarrow z_o$
$\Delta t \leftarrow 0.5*\Delta t$

Figure 6: Flow Chart of Runge-Kutta-Fehlberg Algorithm

Two variants of the bisection method are used for functions known at discrete points. The first of these is used to find between which two entries in an array another value lies for the purpose of interpolation. This is used extensively in computing the saturations at various depths in profiles, from values on characteristics. An efficient binary search technique was implemented for this purpose (the method was based on a routine appearing in Forsythe, Malcolm and Moler, 1977, pg. 79). The second is used in cases where many bisection solutions would be made of the same function. To save computational effort for these functions, a set of 50 function values are saved at the beginning of the program. When the inverse of the function is needed, a binary search is done on the saved values, and inverse quadratic interpolation (Abramowitz and Stegun, 1965, pg. 882) is used to determine the interpolated value.

Functions are integrated with a 7 point Gauss Quadrature routine (Abramowitz and Stegun, 1965, pp. 887, 916). This was chosen to provide reasonably high accuracy, while utilizing relatively few function evaluations. Quadrature is used to obtain the mass of substances in the soil, by integrating the saturation (and concentration) profile. Note that mass balances reported in the discussion of results are obtained numerically, and contain some error.

Both programs produce the following three types of output. First, after echo printing the input data, a record of the locations of the fronts and their saturations, concentrations and mass balances at each point in time of the solution is produced in an output file. Second, in a separate file, concentration and saturation vs. depth profiles for selected times are written. Third, at selected depths, concentration, saturation, and flux histories are written in another file. These provide the user with a record of the flux of pollutants passing a certain depth at each time. Specific details of these and other features of the implementations are presented below.

SECTION 6

MODEL IMPLEMENTATION AND RESULTS

Two implementations of the kinematic model will be presented in this section. First, a simplified implementation is presented that assumes a uniform constant water saturation is present throughout the profile. This model is called KOPT (for Kinematic Oily Pollutant Transport), and is intended to be used as a screening tool for oil spills. It addresses the questions of how far spilled oil might go into the soil and how soon it might get there. In this case, no rainfalls are assumed to occur; the specified water saturation is taken as representative of climatic conditions. This model is usable with other models of subsurface oil transport. Specifically, it can be used to supply input data to the model of oil spread along the water table developed by Roberts-Schultz (1988). This discussion will also be used to introduce the elements of the method of characteristics solution, in preparation for the more complicated variations that occur in the full model.

The full implementation, presented later in this section, includes the effects of rainfall on the spilled oil, and is called KROPT (for Kinematic Rainfall and Oily Pollutant Transport model). It includes the modifications of the kinematic model for water (infiltration and evaporation) discussed above, along with a model for the stochastic generation of rainfall. The character of the results will show that the incoming water has an extreme influence on the flow of the oil. In some cases, the water flux is too high for the kinematic model, and the method breaks down. A discussion of how to generalize the model for these cases is presented in Weaver (1988).

KINEMATIC OILY POLLUTANT TRANSPORT MODEL (KOPT)

In the KOPT model, rainfall is represented by using an average infiltration rate. The corresponding water saturation is determined through inversion of the effective hydraulic conductivity relationship:

$$q_w = K_{ew}(S_w) \rightarrow S_{w(avg)} = K_{ew}^{-1}(q_{w(avg)}) \qquad (48)$$

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which for the water relative permeability (equation 10) is

$$S_{w(avg)} = S_{wr} + (1 - S_{wr})\left(\frac{q_{w(avg)}}{K_{sw}}\right)^{1/\varepsilon} \quad . \tag{49}$$

$S_{w(avg)}$ is used as the water saturation for the entire profile. When q_w is a constant, the phase conservation equation for water shows that $\partial S_w/\partial t = 0$, and the equation is effectively solved.

The oily pollutant is assumed to enter the soil and fill some portion of the pore space that is not occupied by water or trapped air. If the oil leaks at a rate which is less than the maximum rate that the soil can accept, then equation 26 is used to determine the (kinematic) speed of the invading oil. The oil's effective hydraulic conductivity, which is equal to its flux rate in the kinematic model, is inverted to obtain the oil saturation during the application, $S_{o(max)}$. In doing this, the average water saturation, $S_{w(avg)}$, is used in all the oil equations.

When the application rate of the oil exceeds the kinematic capacity of the soil, the Green-Ampt (Green and Ampt, 1911) model can be used for the oil flux. For cases with applied head of H_s,

$$q_o(S_{o(max)}) = K_{eo}(S_{o(max)})\left(1 + \frac{H_s}{z_f}\right) \tag{50}$$

where z_f is the depth to the oil front. Initially the pressure gradient H_s/z_f is infinite, because z_f is zero, but is reduced as the oil front invades the soil. The head H_s may be due to surface ponding and/or capillary pressure. This situation adds a constant head boundary condition to those shown in Table 1. Even though there is a head applied at the surface, the amount of water in the soil is unchanged in this situation, as the water saturation is considered representative of climatic conditions.

In cases where the supply of the oil is finite, the kinematic model ties in with the end of the oil event to model the drainage. Drainage modeling is not possible in a ``pure'' Green-Ampt model and is a special feature of the present model.

The solution is obtained in the following manner. The flux from equation 50 or the kinematic flux is used in the jump equation, 26, to give the oil front speed,

$$\frac{dz}{dt} = \frac{q_o(S_{o(max)})}{\eta \, S_{o(max)}} \qquad (51)$$

The method of characteristics solution (equation 20 and 21) is used to give the characteristic directions: either through inversion of the derivative of the relative permeability curve when λ_o is zero, or by solution of the differential equations when λ_o is not zero. The distribution of the constituent is obtained from the method of characteristics solution of the constituent equations (32 and 33), and the volatilization model (equation 44). The constituent moves at rates that are determined by the partitioning phenomena, and the speeds of the oil and the water. There can be an apparent cleansing of the oil. This can be in front of the constituent's maximum depth, if the constituent moves slower than the oil. If the oil moves slower than the constituent, then the constituent can be leached entirely out of the oil. In reality dispersive forces and non-linear partitioning smear the assumed sharp constituent fronts, and so make the cleansing less complete.

A brief example of oil migration will be presented to introduce the types of results obtainable from the model. More examples are presented in following sections. Figure 7 shows the base characteristic plane and the projection of a few displacement paths in z-t space. Shown here is the result of a sixty day simulation from a ten day oil release at 2 cm^3/cm^2/day into a dry sand. Other details of this case (example 1) are found in Table 2. During the oil release, the oil fills 37.6% of the pore space and moves at its maximum speed. This is indicated by the straight line labeled AC on Figure 7.

Once the supply of oil ends, drainage begins and there is in the profile a region of constant oil saturation (triangle ABC), associated with the oil release, that will now be replaced by a region of variable saturation, associated with the method of characteristics solution for oil drainage. The displacement path (called a characteristic) of the residual saturation, S_{or}, remains at the surface, because its speed is zero by definition. Bounding the region of maximum saturation, ABC, is the characteristic corresponding to $S_o = S_{o(max)} = 0.3458$. In between are characteristics for all intermediate values of S_o. They are represented in the figure by characteristics for each 0.01 increment of oil saturation. The greatest oil saturations are found the deepest in the profile, because the derivative of the k_{ro}

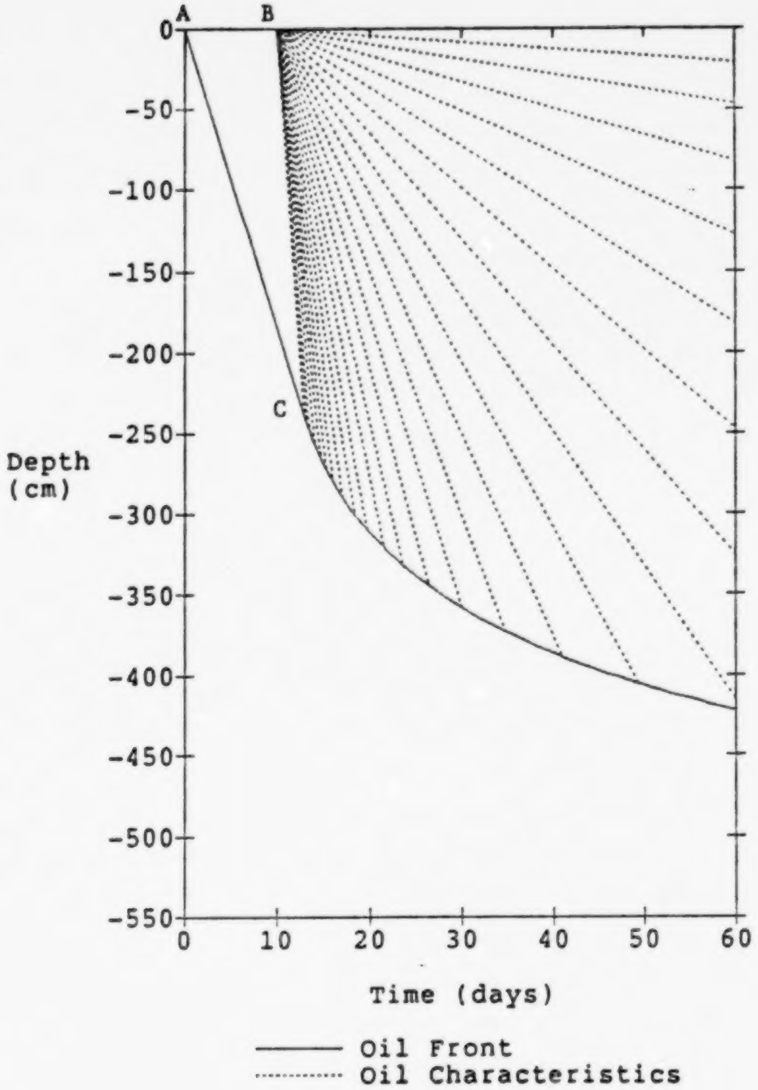

Figure 7: Oil Spill in a Fine Sand

Table 2: Input Data for Examples 1, 2 and 3

		Example 1	Example 2	Example 3
Soil (a)		Fine Sand	Silt Loam	Sandy Clay Loam
K_{vs}	cm/day	209.7	39.4	118.5
λ		3.7	0.207	0.3446
η		0.314	0.462	0.328
ρ_b	gr/cm^3	1.72	1.70	1.70
f_{oc}	%		1	1
Water				
S_{wr}		0.1669	0.039	0.2287
q	cm/day	0	0.015	0.104
u	gr/cm/day	872	872	872
Oil				
u	gr/cm/day	1285	471	1000
ρ	gr/cm^3	0.73	0.65	0.65
S_{or}		0.10	0.05	0.10
half life	days		360	180
lag time	days		45	30
loading	cm/day	2.0	1.0	
time	days	10	25	
volume	cm^3/cm^2			1.7
depth	cm			30
Constituent				
C_o(init)	mg/l		200	200
half life	days			360
lag time	days			45
k_o			134 (b)	50
k_h			0.15 (b)	0.10
k_{oc}			60 (b)	10
Climate				
Temperature	°C		20	15
Evaporation	cm/day		0.1	0.15
Relative Humidity			0.5	0.5

a) Example 1 soil data from Brooks and Corey, 1964; Example 2 & 3 soil data from Brakensiek et al., 1981
b) from Ryan et al., 1987

function is such that the highest oil saturations have the highest speeds. Thus the pattern of characteristics which determines the shape of the oil profile results from the method of characteristics solution of the oil equation and the relative permeability function. This pattern is called a centered simple wave.

Figure 8 shows oil profiles for 10, 11, 30 and 60 days. In these and all subsequent profiles, water and the total liquid saturations are plotted, and the oil saturation is read as the difference between the two. At 10 days the profile has not yet begun to drain and the oil saturation is equal to 0.3458 at every point above the oil front. By 11 days drainage is occurring from the surface down to a depth of 80 cm. The region from 80 to 202 cm still has the original saturation of 0.3458. Once the oil saturations that are less than $S_{o(max)}$ reach the oil front, then its speed begins to be reduced in accordance with equation 26. As time goes on the speed of the front slows as it intersects slower and slower characteristics. Figure 8 also shows the oil profile for 30 and 60 days where the entire profile is undergoing drainage, and the oil front saturations have dropped to 0.2201 and 0.1809, respectively. In the kinematic model it is only after an infinite amount of time that the oil saturation is at residual throughout the entire profile at which time, the motion of the front stops. Practically, however, the speed of the front becomes negligible at much shorter times. When this occurs the depth of the front, and thus the depth of the entire oil contaminated zone, z_{ocz}, is given by the simple calculation,

$$z_{ocz} = \frac{\Delta t_o q_o}{\eta S_{or}} \tag{52}$$

where q_o is the application rate of oil, and Δt_o is the duration of the oil spill. Equation 52 gives the ultimate depth of a nondegrading oil. It is a useful quantity, if the residual saturation is known.

As noted previously, the relative permeability functions are subject to hysteresis. Solution of the kinematic model shows that, where the classical method of characteristics solution holds (equations 20 and 21) drainage is occurring in the oil profile (see Figure 8). The drainage relative permeability model (eq. 11) applies to this situation. Imbibition (or oil wetting) occurs at the oil front. The true shape of the oil profile at the oil front is determined by imbibition relative permeability and capillary pressure functions. An imbibition relative permeability curve is necessary for modeling this shape. In this model, however, the shape of imbibing profile is not modeled, as the front is assumed sharp. The

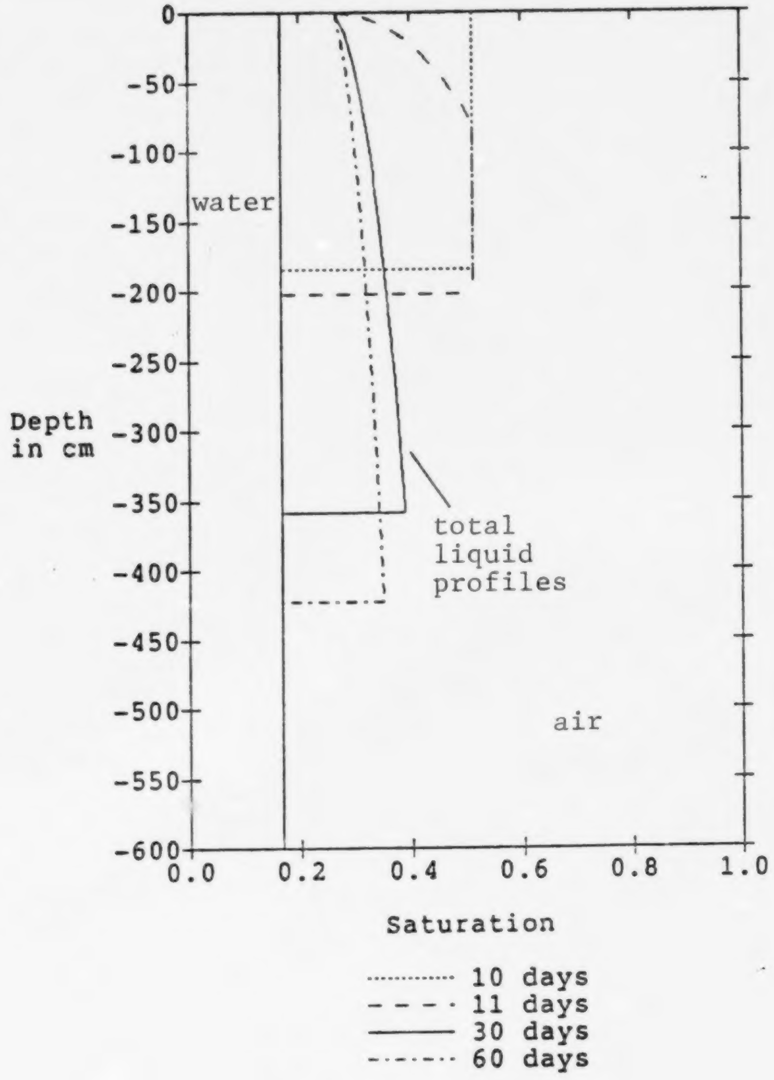

Figure 8: Oil Profiles

consideration that must be addressed is the speed of the front, which is determined by the hydraulic conductivities on either side of the front. Since the hysteresis loops connect the drainage and imbibition capillary pressures at the point where the draining profile becomes an imbibing profile the relative permeability is the same. The imbibing k_r is not necessarily the same as the drainage k_r, since a scanning loop connects the drainage and imbibition curves. The drainage k_r is in error over the range of saturations where the capillary pressure follows the scanning loop. The error is expected to be within the same range as those caused by the other assumptions of the model, since the magnitude of the difference between imbibition and drainage k_r is often $< 10\%$.

KOPT Model Results

Example 1: Oil Spill into a Fine Sand--

Figure 9 shows the maximal extent of the oil for the same oil loading as in Figure 7, but extended for 180 days. For clarity none of the characteristics are shown, but the oil saturations vary as discussed for Figure 7. The maximum numerically computed volume balance error for the oil is 0.15% and occurs at 180 days. Also shown in Figure 9 is a simulation where the oil has a half life of 180 days in the soil. Note that for both cases most of the total depth achieved is done so in the first 20 days of the simulation. However, during the first few days there is virtually no difference between the two cases. At those short times (relative to the half life), the decay does not significantly reduce the effective hydraulic conductivity of the oil. Later as the decay becomes significant, the front for the decaying oil slows. The KOPT model also allows a lag time to be incorporated to account for acclimation of soil micro-organisms (see Table 2). In contrast, the non-decaying oil continues to move downward throughout this time, reaching a depth of 504.7 cm at 180 days, 101.9 cm deeper than the degrading oil. Equation 52 predicts the final depth for this case to be 796 cm, which will not be achieved by the degrading oil.

Profiles at 60 and 180 days are drawn in Figure 10. At 60 days and for the decaying oil at depths above 3.5 cm, all the oil has been reduced to saturations below residual and is thus immobilized. The oil's decay is creating a region of immobilized oil in the profile. This begins at the ground surface and works downward with time. The dotted line on Figure 9 shows the locus of points where decay has reduced the oil saturations below residual. Thus all points above and to the right of this curve are at oil saturations at

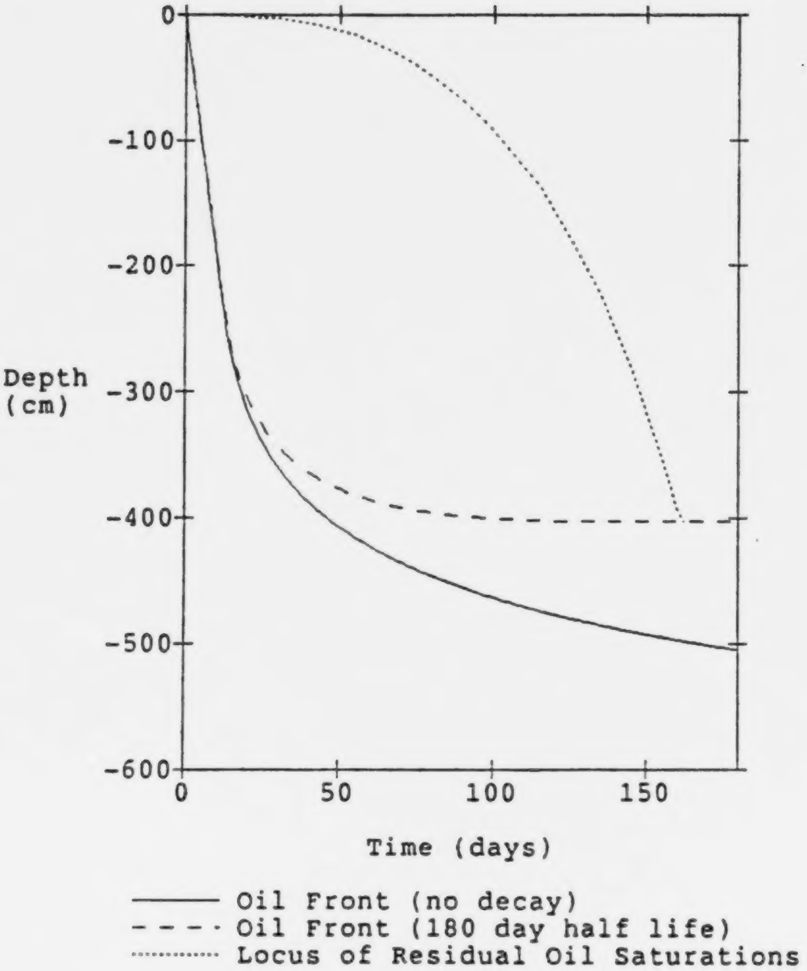

Figure 9: Example 1 - Base Characteristic Plane for Oil Spill in Fine Sand, 180 Duration

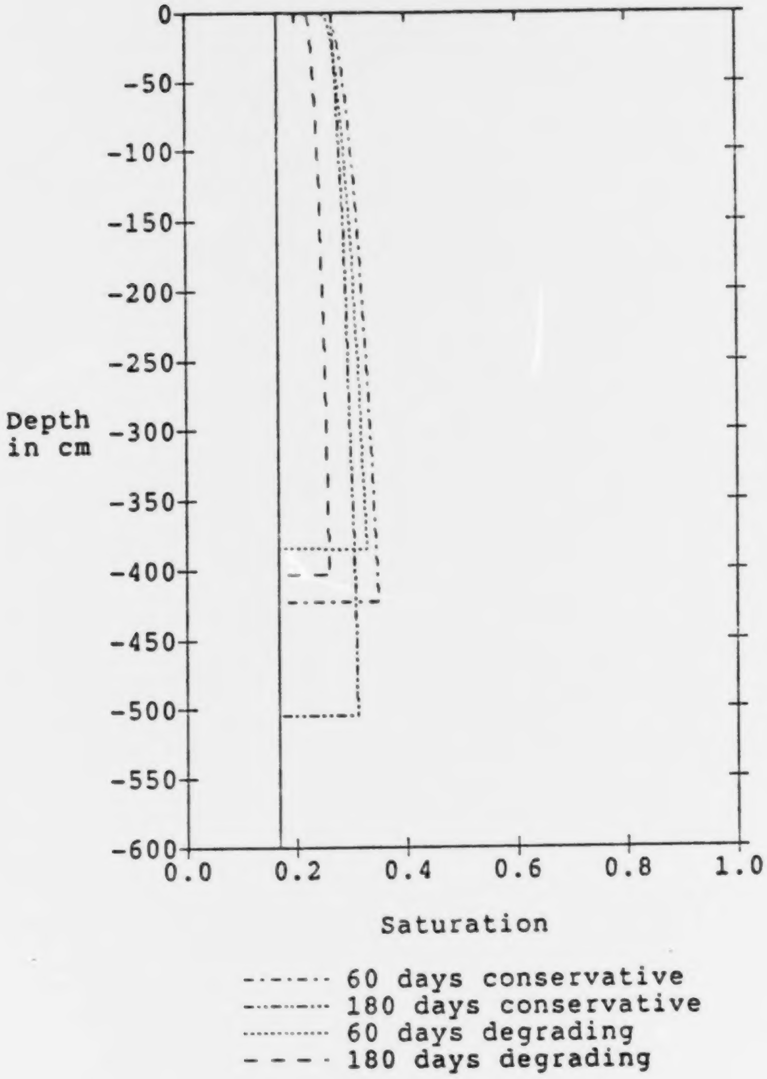

Figure 10: Example 1 - Conservative and Decaying Profiles at 60 days and 180 days

or below residual. At approximately 160 days the oil saturation at the front is reduced to residual and all motion of the oil stops.

The sensitivity of the solution for the nondecaying oil to the magnitude of the residual oil saturation is shown by Figure 11. All parameters of example 1 were unchanged, except for the residual oil saturation. The greatest depths were attained for the smallest residuals. This result is due directly to the increased oil relative permeability at a given oil saturation, with decreasing residual oil saturation (equation 11).

Example 2: Gasoline Leak into Silt Loam--

The next example is of a gasoline leak in a silt loam soil (Table 2). The water flux is 0.055 cm/day (20 cm/year), which results in a water saturation in this soil of 0.6108. A constituent initially present in the gasoline at 200 mg/l is partitionable into the water and slightly sorbed. The partition coefficients are for benzene (Ryan et al., 1987). When placed in the soil, the concentration in the gasoline instantaneously changes to 199.70 mg/l, according to the flux relationship (equation 39). The water concentrations are 134 times lower than these values, according to the partitioning relationship. If only water samples were analyzed, much of the mass of the constituent would be missed.

For a volatile constituent ($k_h = 0.15$), the upper boundary is indicated as ``volatile front" in Figure 12. The mass balance for the constituent is shown in Figure 13, where the sum of the mass remaining in the soil and the mass volatilized is seen to remain very close to the amount placed into the soil (0.5 mg/cm). The maximum mass balance error for the constituent is 0.3%. Volatile losses are calculated using the volatilization model described above. Profiles for the volatile constituent are shown in Figure 14. These show that the contaminated zone moves downward with time, and that concentrations increase throughout the simulation. The concentrations are calculated by equation 35, which models the effect of oil decay on the constituent concentration. The mass balance indicated in Figure 13 includes the increase in concentration. The limiting constituent concentration in water is 24.28 mg/l. None of the concentration profiles contain this value, since the oil is present throughout the simulation. The decaying oil profiles are shown in Figure 15.

Gasoline is highly volatile, because of the large amounts of volatile constituents it contains, so some loss of the liquid is expected. This model (and also the KROPT model)

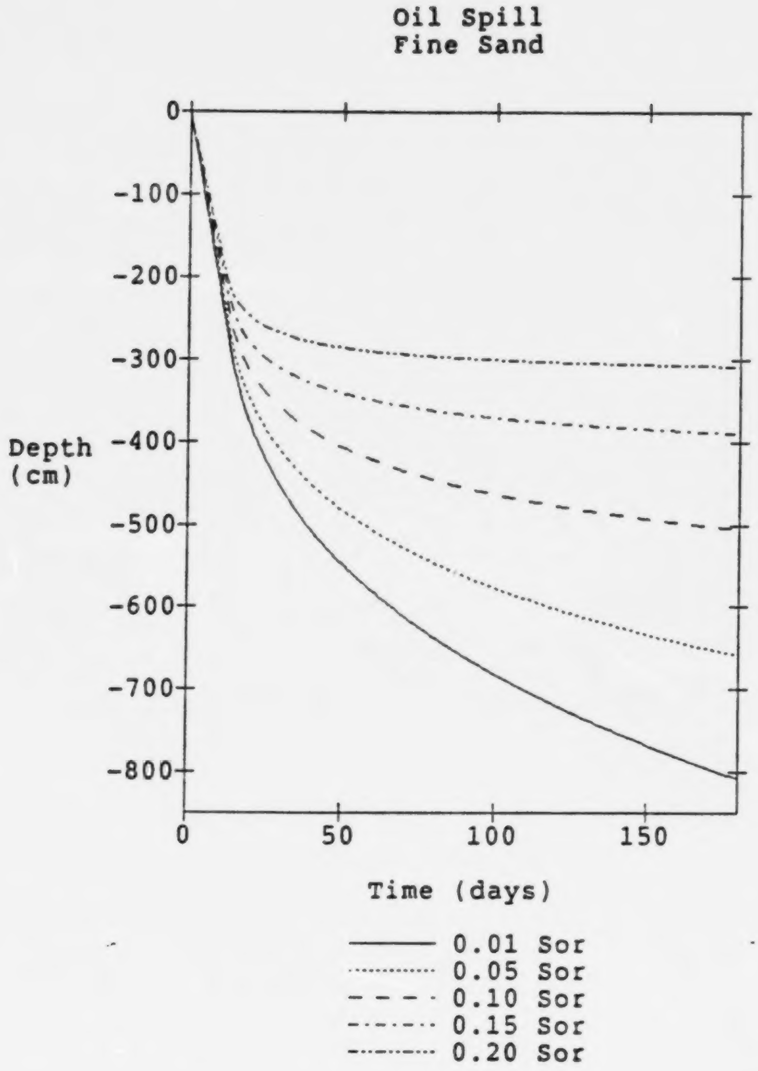

Figure 11: Sensitivity of Results to Residual Oil Saturation

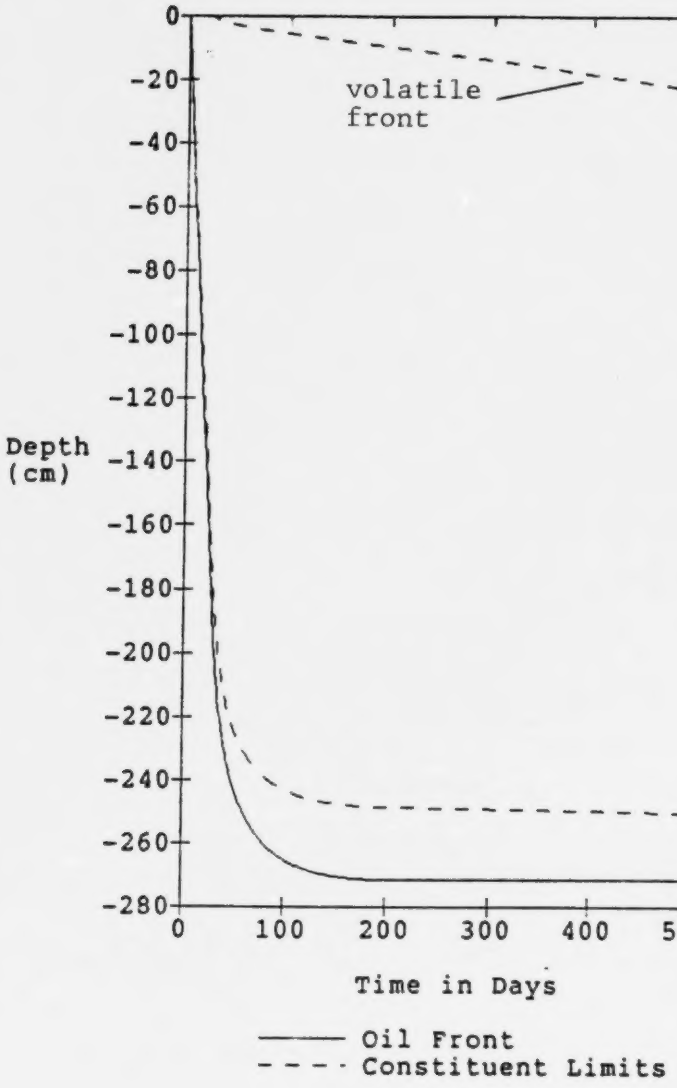

Figure 12: Example 2 - Base Characteristic Plane

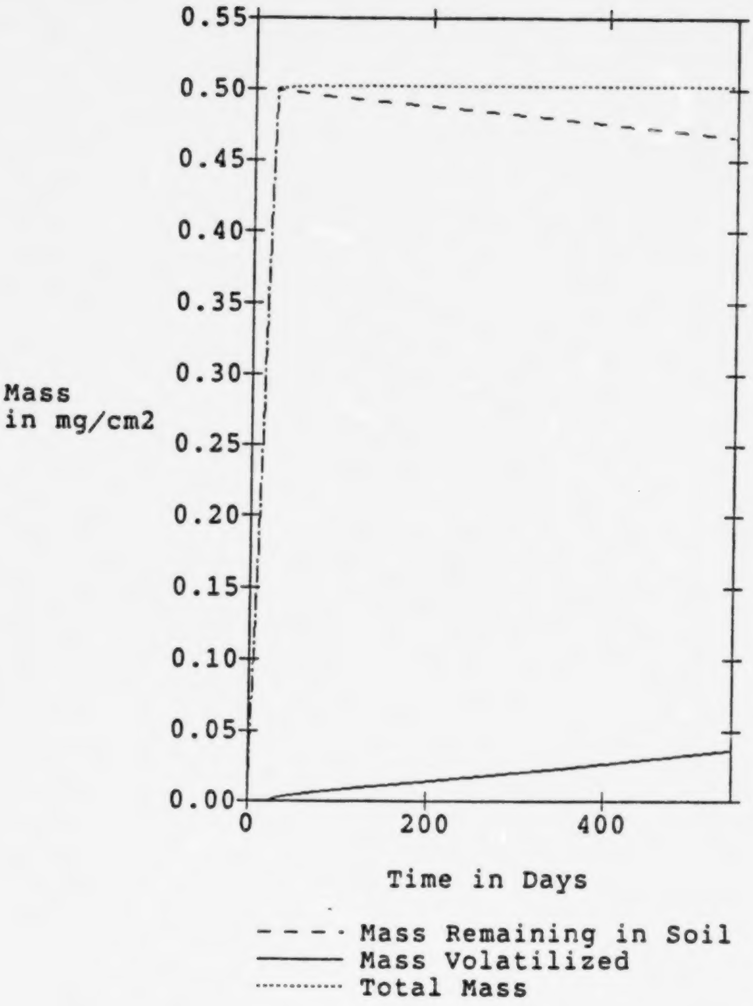

Figure 13: Example 2 - Constituent Mass Balance

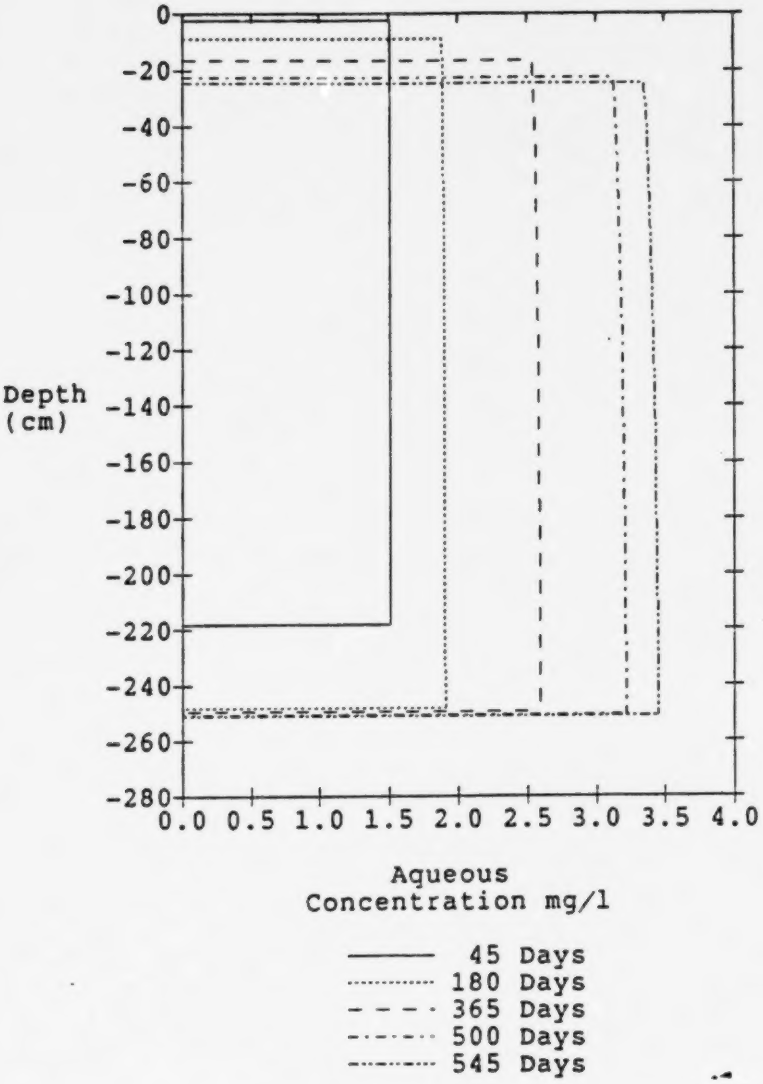

Figure 14: Example 2 - Concentration Profiles

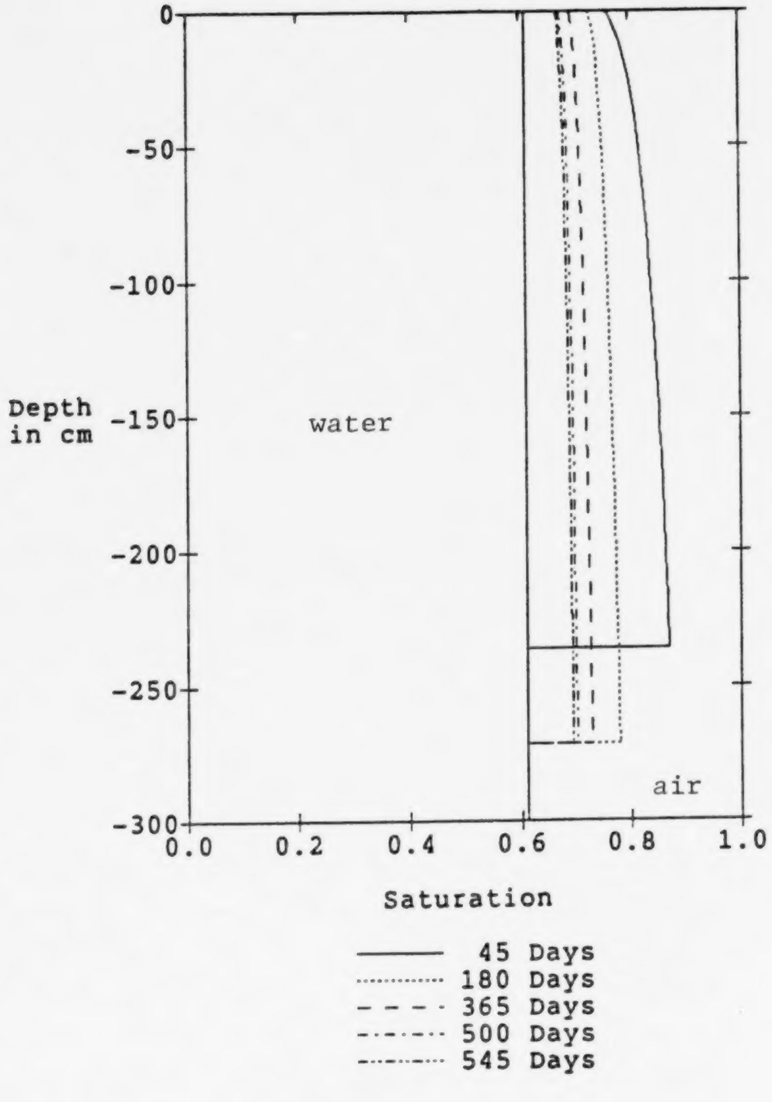

Figure 15: Example 2 - Oil Profiles

are not suited for modeling the loss of the immiscible liquid. Only the volatile loss of a dissolved constituent is considered. Some loss of the gasoline is expected, but the model results are conservative for these applications insofar as no loss of gasoline gives the maximum amount of gasoline in the soil.

Example 3: Land Treatment in a Sandy Clay Loam--

A hypothetical land treatment example is presented in Figures 16 - 20. There are 330 barrels of oil per acre (1.70 $cm^3/cm^2/day$), corresponding to the maximum typical industrial loading reported by Ryan et al. (1986), uniformly placed in the top 30 cm of the soil. Since its maximum saturation is above the residual (0.1727 vs. 0.1000), the oil moves 12.7 cm out of the bottom of the plow zone before it is immobilized. If the oil were nondegradable, equation 52 indicates that it would have moved 22 cm out of the plow zone. With a half life of 180 days, 30 days required for acclimation, and constant residual saturation of 0.10 assumed, the oil is immobilized after 104 days.

The vertical extent of volatile constituent is indicated in Figure 16. The infiltrating water leaches the constituent from the oil. After 455 days all of the constituent is deeper than the now immobilized oil. Once this happens all constituent characteristics are straight lines, since the motion is only due to the water flux, and there is no oil present (see equation 33). Where the constituent is above the oil front, the characteristics' curvature (as evidenced by the dotted line) is caused by partitioning into the degrading oil. In this case and as would be typical for land treatment, the oil only moves a small distance. Its motion has a minimal effect on the ultimate migration of the constituent.

Concentration profiles for times from 30 to 730 days are presented in Figures 17 and 18 for the nonvolatile case. At 30 days the concentration is equal to the initial value throughout the profile, since neither the oil nor the constituent have started to decay. At 60 days biodegradation of the constituent has reduced the concentration at the leading edge, while concentrations above the oil front are increased because of oil biodegradation. The straight line connecting these values is an artifact of the number of characteristics used for the constituent. At 30, 60 and 180 days only one constituent characteristic is below the oil front and linear interpolation is used to find intermediate concentrations. By 270 days enough characteristics are below the oil front to give the profile curvature. The general

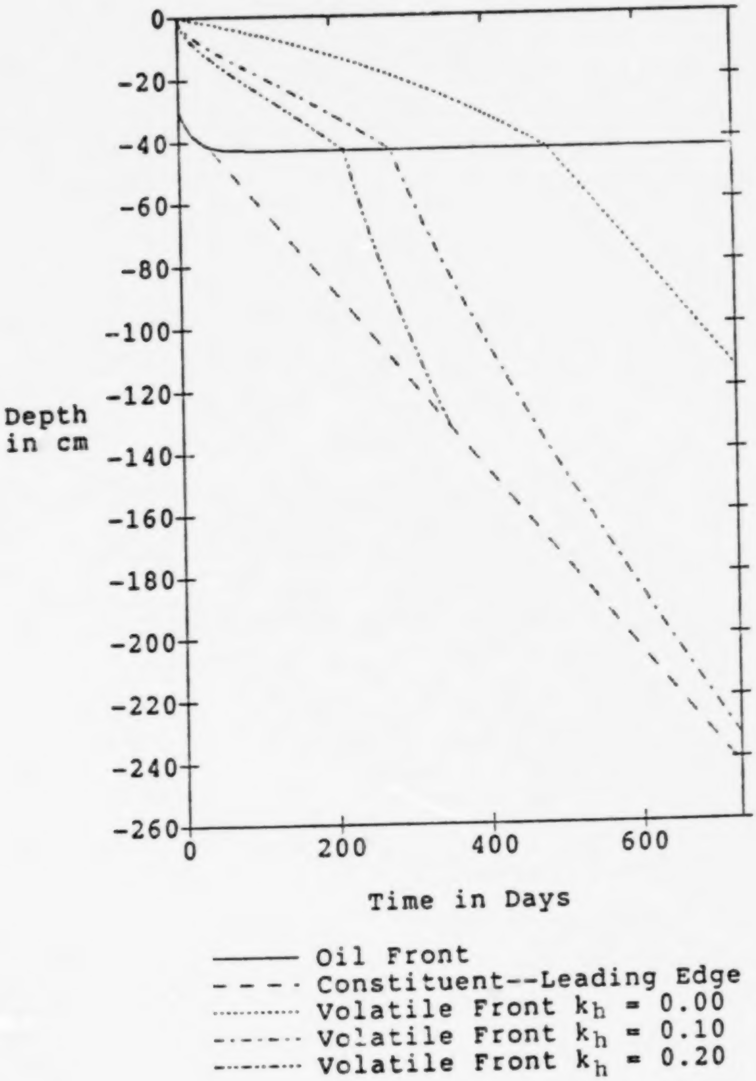

Figure 16: Example 3 - Base Characteristic Plane

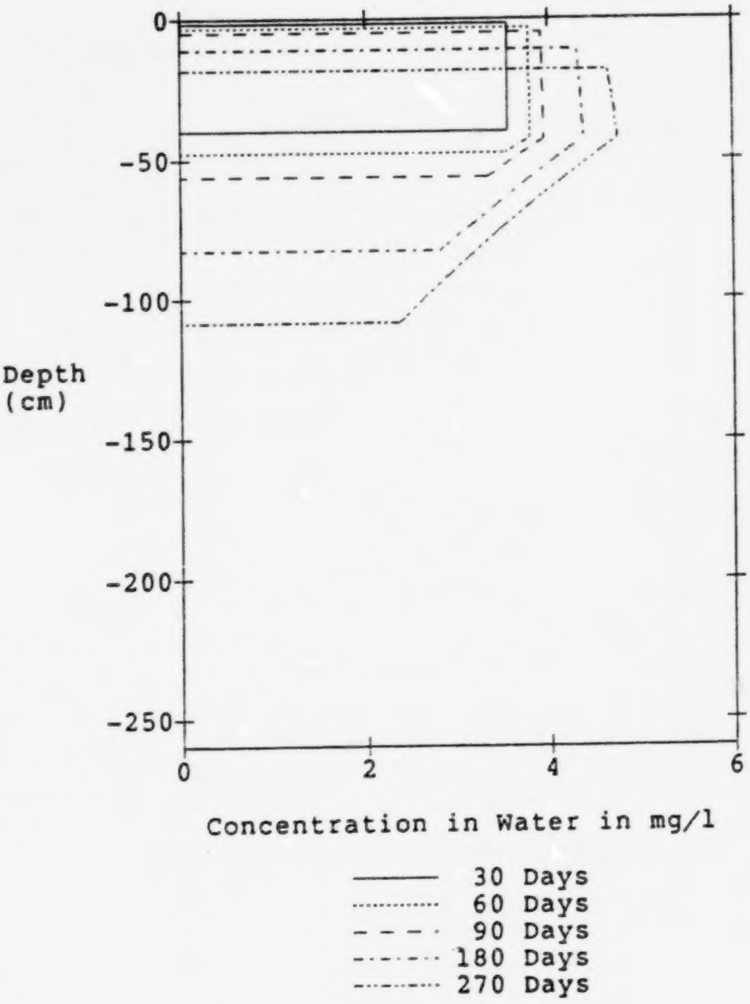

Figure 17: Example 3 - Concentration Profiles

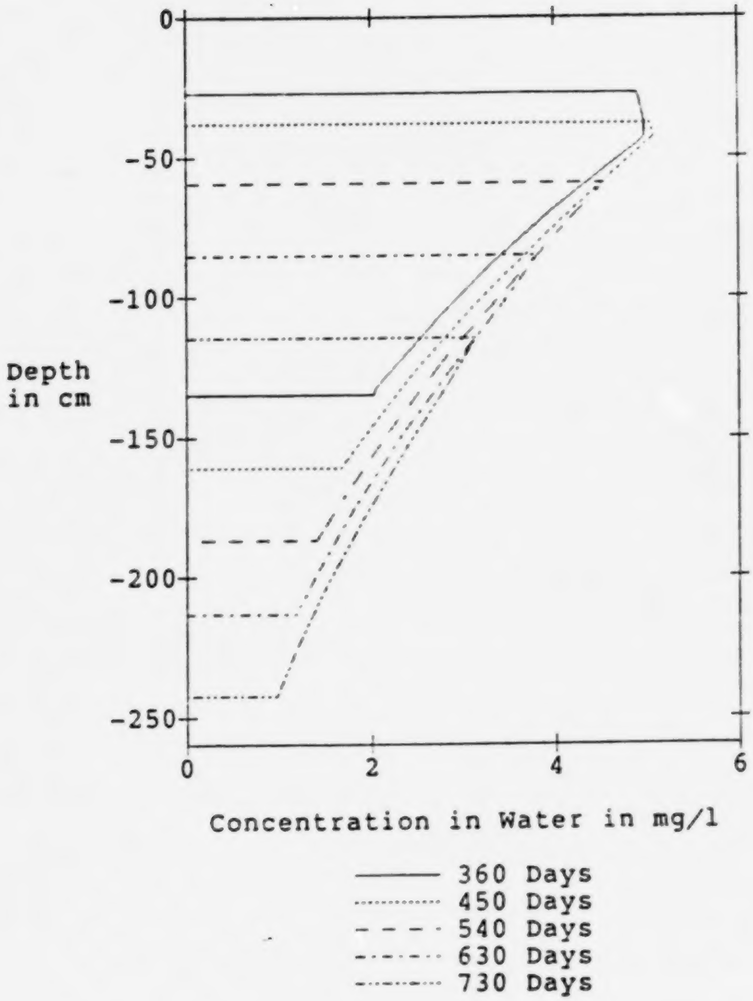

Figure 18: Example 3 - Concentration Profiles (continued)

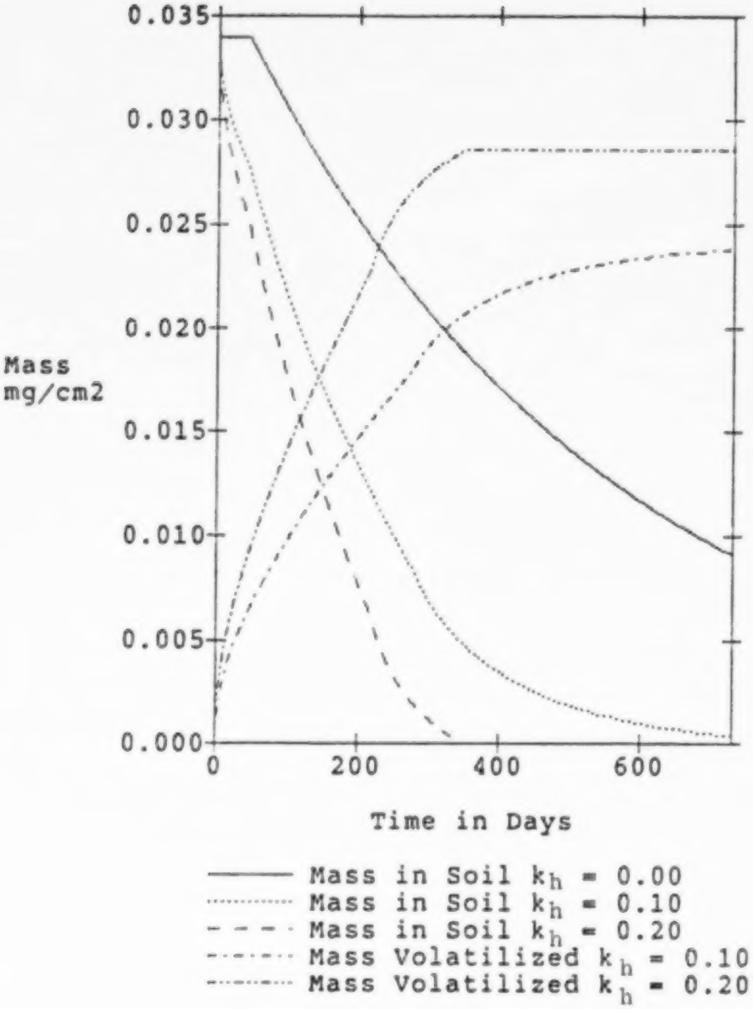

Figure 19: Example 3 - Volatilization Comparison

trend of the 60 and 90 day profiles continues until the constituent is entirely ahead of the oil front (at 455 days). All concentrations then decrease due to constituent biodegradation.

The same case was run with $k_h = 0.1$ and $k_h = 0.2$ to illustrate the effects of volatilization. The solid line in Figure 19 shows the nonvolatile case. The mass begins to be reduced after the lag of 45 days has ended. At 405 days, one half of the constituent's mass is gone. This corresponds to the half life of 360 days. Volatilization reduces the mass in the soil further. Note that for both volatile cases shown, there is more total mass (mass volatilized + mass in the soil) than for the nonvolatile case. This is because volatilized constituent has left the soil and cannot be degraded. It is only the remaining fraction of the mass that is subject to degradation.

Concentration histories are shown in Figure 20. At the bottom of the plow zone (30 cm), the concentration is at the initial value (equation 40) until the oil degradation lag ends. The kink in the concentration history curve occurs when the constituent biodegradation begins (after 45 days). Thereafter the concentration increase caused by oil biodegradation is reduced by constituent biodegradation. In this case the half life of the oil is the shortest, so that the concentrations always increase in the presence of decaying oil. This occurs until the water leaches the constituent out of the plow zone at 501 days. After 400 days the constituent reached 150 cm in depth (approximately the depth to the lower treatment zone). Lower concentrations are encountered, since oil biodegradation no longer inflates the concentrations.

KOPT Model Implementation

The specific details of the implementation of the KOPT code are presented in Weaver (1988). The programming synopsis is shown in Table 3. For each step in time, the right hand sides of the oil equations are evaluated first. As the RKF routine performs each intermediate step, the oil solution must be known before the constituent equations are solved. There is storage space reserved for the oil front and oil characteristics. The oil characteristics are only solved when the oil is biodegradable. Otherwise the solution of the oil characteristics are straight lines which need not be evaluated numerically. A set of 51 characteristics is used for the oil. Ten of the set are used during the oil's application and the remaining 41 are used for the drainage pattern.

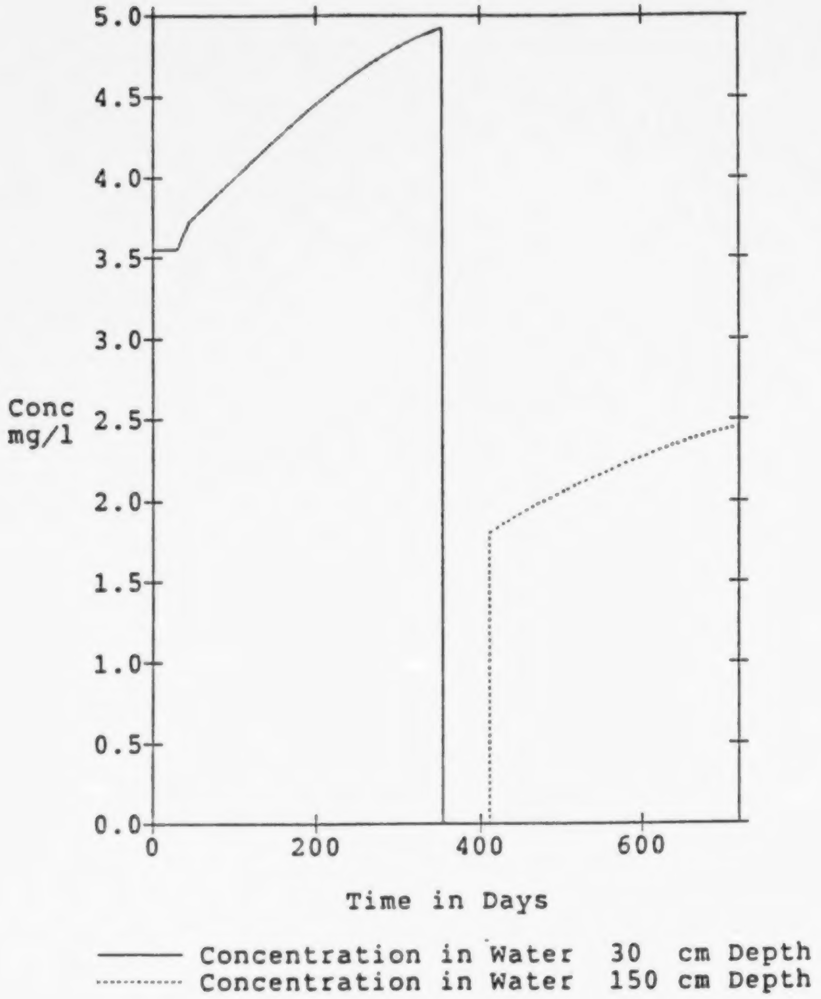

Figure 20: Example 3 - Concentration Histories at 30 and 150 cm Depths

Table 3: KOPT Programming Synopsis

Equation	Fronts	Charactertstics	Notes
Water	0	0	Constant value used
Oil			
Nondecaying	1	0	
Decaying	1	51	10 characteristics used during oil release 41 characteristics used for sinple wave
Constituent			
nonvolatile	0	11	
volatile	1	11	Front is for the volatilization model

Item	Controller Checks	Notes
Water	None	
Oil	Beginning of Event	
	End of Event	
	End of $S_{o(max)}$	See figure 4.1, point B
	At least 5 steps through release	Nondecaying oil
	Starting time of each characteristic	Decaying oil
Constituent	Time when characteristic passes oil front	
	Volatilization of entire mass of const.	Remove all constituent equations
Simulation		
	Place solution on even time step	
	Simulation Ending time	
	Profile times	

For cases with nondegrading oils, no oil characteristics need to be computed by the RKF solver, since they are straight lines. This makes for a very efficient solution as only one equation is needed to determine the oil solution (that for the front). If the oil is biodegradable, all oil saturations decrease with time. Thus the speed slows down and the characteristics bend, in accordance with equation 21. Characteristic speeds are still given by equation 21, but are time dependent according to equation 22 and the k_{ro} function. Points defining the curved characteristics must be stored temporarily, since equation 26must be used to determine the speed of the front. Note that many characteristics are used to determine the solution initially, but as time goes on fewer and fewer are used in the solution. At later times, however, the oil profile is flatter and thus the loss in accuracy due to fewer characteristics is offset by the shape of the profile to some degree.

This problem does not exist for a nonvolatile constituent, since the linearity of the solution assures that characteristics never intersect the leading edge of the discontinuity. Thus the solution is always determined by the same number of characteristics. The equations for these are solved last, since the oil and water saturations and fluxes must be known. Eleven characteristics are used for the constituent. Since the constituent equation is linear under the model assumptions, no equation is needed for a front; the deepest characteristic corresponds to an invading discontinuity in concentration. One equation is used for the volatilization model.

KINEMATIC RAINFALL AND OILY POLLUTANT TRANSPORT - (KROPT)

In this section the implementation of the kinematic model for flow of both the water and oil is presented. Instead of using constant water saturations and fluxes, the unsteady migration of water is also modeled. This makes the model more realistic by considering the effect of a series of rainfall events on the oil and the dissolved constituent.

The Formation of Oil Banks

A difficulty of the method of characteristics solution approach for this problem is that the qualitative nature of the solution must be determined in advance by the programmer (i.e., not by the user). The classical method of characteristics solution does not indicate where discontinuities appear. If the proper discontinuities are not included, then the solution fails to conserve mass. A crucial example occurs as water begins to infiltrate into the soil. Ahead of the water front, the water saturation is at some pre-existing value, while behind the water front it is determined by the incoming water. Oil moving at constant flux across the water discontinuity would also experience a change in saturation, due to the dependence of oil relative permeability on water saturation (Figure 3). At the location of the water front, there is a discontinuity in the oil saturation. This means that both saturation derivatives in the oil (equation 18) fail to exist at the water front, implying that the jump condition (equation 26) must be applied to the oil.

The speed of the jump is fixed by the water front speed in the kinematic model, and the upstream oil saturation is fixed by the boundary condition. The oil saturation ahead of the water front, then, will depend on these two. At some point further just ahead of the water front, the oil saturation is again a value determined by the boundary condition of the problem, since it is as yet unaffected by the invading water. Thus there is a second transition (which is also a jump) down to the saturation at the deeper depth. This phenomenon also occurs during oil production activities (e.g. Helfferich, 1981), where the region of increased oil saturation is called an oil bank. Oil banks will be discussed at length in the following section. Control volume analyses of oil banks for steady and unsteady flows are presented in Weaver (1988).

Quasi Steady Oil Banks--

The first step in studying the oil bank phenomena is to consider a simplified case where there is no drainage. In such a situation the method of characteristics solution plays no role, and the jump equations can be studied by themselves. As an example, oil is applied at a constant rate for ten hours to a sand where water is at residual saturation throughout the profile. Five hours later, additional water begins to infiltrate, also at a constant rate. Figures 21 and 22 show the base characteristic plane and a profile for this case. Table 4 contains the input data used.

Ahead of the water front (line BH on Figure 21), the relative permeability of the oil is subject to a water saturation of S_{wr} (0.1669). The oil flux (0.2 cm/hr) gives, through inversion of the hydraulic conductivity for oil, the oil saturation, S_{o3}, as 0.3730. Down to the depth of the water front, the water saturation is $S_{w(max)} = 0.4536$, determined by

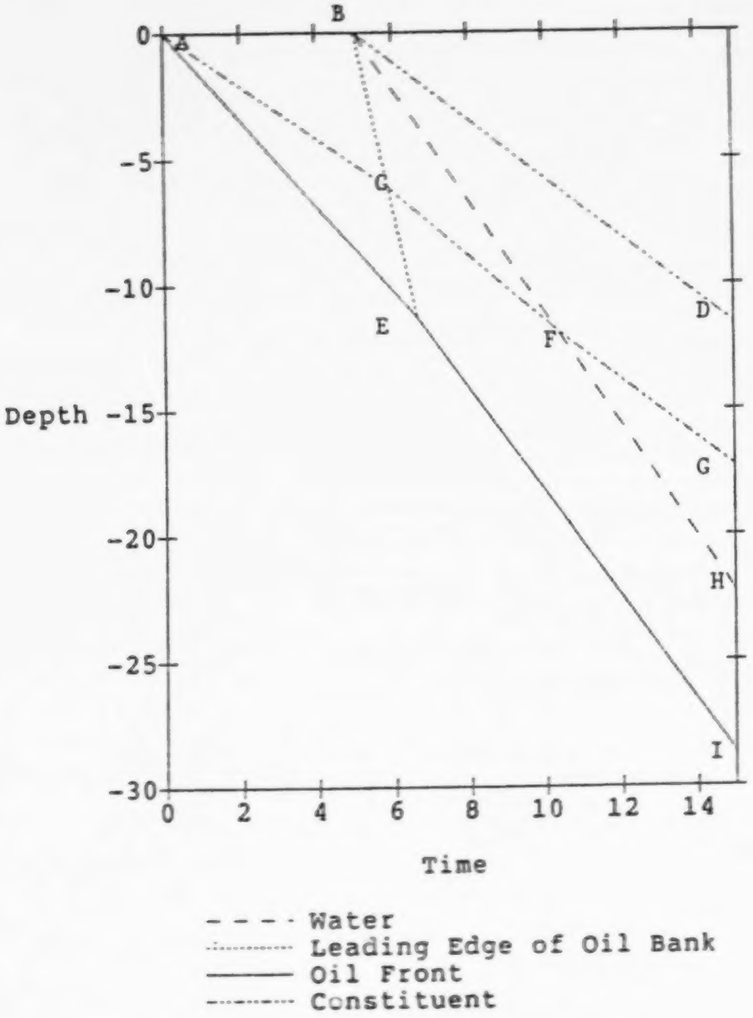

Figure 21: Quasi-Steady Oil and Water Migration

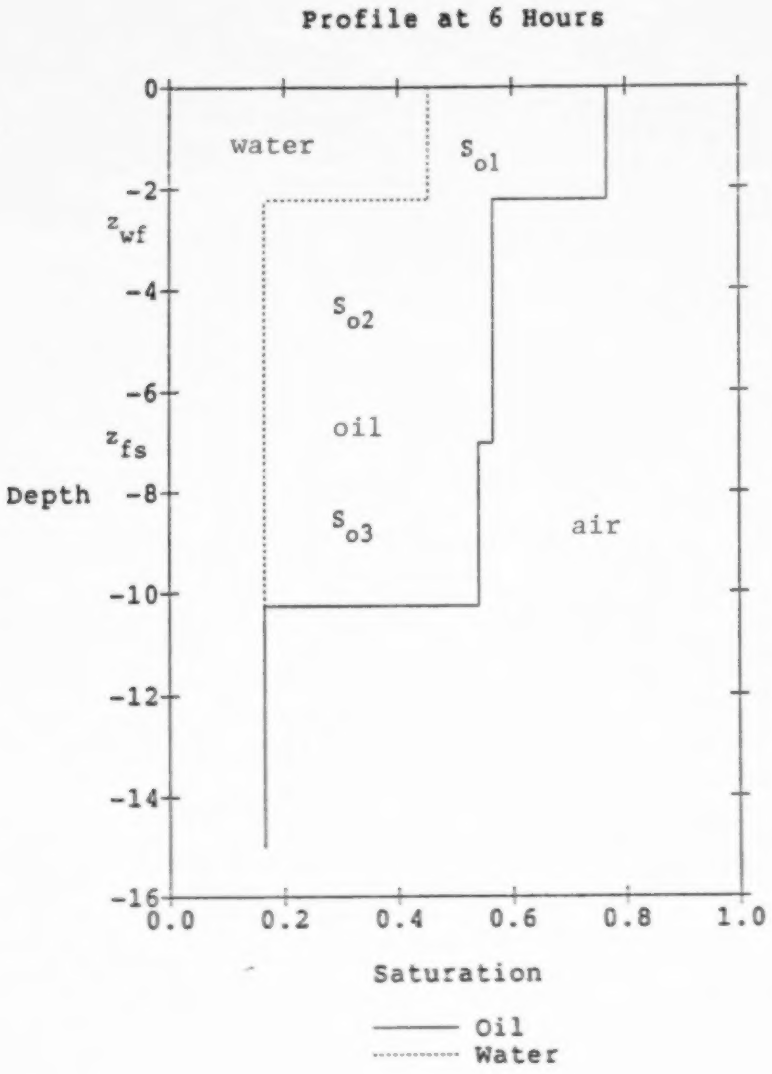

Figure 22: Quasi-Steady Oil Profile

Table 4: Input Data for Steady State Oil Bank Discussion

Soil			Fine Sand
	K_{ws}	cm/hr	8.74
	λ		3.7
	η		0.314
	ρ_b	gm/cm^3	1.50
	f_{oc}		0.01
Water			
	S_{wr}		0.1669
	μ	gm/cm/hr	36.36
	loading	cm/hr	0.2
	time	hr	1
Oil			
	μ	gm/cm/hr	55.44
	ρ	gm/cm^3	0.73
	S_{or}		0.02
	loading	cm/hr	0.2
	time	hr	1
Constituent			
	C_o(init)	mg/l	100
	k_o		200
	k_{oc}		10

inversion of hydraulic conductivity for water. The boundary between the two regions is the discontinuity, which moves at the speed of the water front:

$$\frac{dz_{wf}}{dt} = \frac{K_{ew}(S_{w(max)})}{\eta(S_{w(max)}-S_{wr})} \tag{53}$$

Applying the jump equation to the flow of the oil, with the speed fixed, prescribes a relationship between the oil saturations on either side of the water front as follows:

$$\frac{dz_{wf}}{dt} = \frac{dz_{rb}}{dt} = \frac{K_{eo}(S_{o2},S_{wr})-K_{eo}(S_{o1},S_{w(max)})}{\eta(S_{o2}-S_{o1})} \tag{54}$$

The oil saturation behind the water front, S_{o1}, can be determined, since the oil flux at the surface remains the same. Inverting the relative permeability function gives this value (0.3149). Since the effect of the water is modeled as causing an increase in the permeability of the medium to oil, then this new oil saturation will be less than the original oil saturation, S_{o3} (0.3730). This indicates that a lower oil saturation is required to give a certain flux, when the water saturation is increased.

A second jump is created, that is, a jump from S_{o2} down to the original oil saturation, S_{o3}. The speed of this jump is given by

$$\frac{dz_{fb}}{dt} = \frac{K_{eo}(S_{o2},S_{wr})-K_{eo}(S_{o3},S_{wr})}{\eta(S_{o2}-S_{o3})} \tag{55}$$

The space between the two jumps (region BEIHF on Figure 21) is an oil bank. The speed of the second jump must be faster than the speed of the first for this solution to make sense. Figure 23 shows the speed of the water front (rear of the oil bank) compared with the front the oil bank. Only one k_r curve is illustrated here, as the water saturation ahead of the water front is constant. The lines drawn on the curve are directly proportional to the speed of the fronts (see equation 26). As long as S_{o2} is also constant, the increase in oil saturations from S_{o1} to S_{o3} assures that the speed of the front of the bank is greater than speed of the rear, 7.03 cm/hr and 2.22 cm/hr, respectively.

Examination of the saturation profile in Figure 22 reveals that the volume of oil that would have been in the region where water is present ($z_{wf}\,(S_{o1}-S_{o3})\,\eta$) is exactly balanced by the extra oil in the bank ($(z_{fb}-z_{wf})\,(S_{o2}-S_{o1})\,\eta$). In effect the infiltration of the water is causing this amount of oil to be displaced in front of the water. Eventually the front of the oil bank overtakes the original oil front and S_{o3} disappears from the profile. Later the water front overtakes the front shock and S_{o2} in turn disappears.

The solution was obtained by using only the jump equations (for the water front, the leading and trailing edges of the oil bank, and the oil front), without resorting to volume

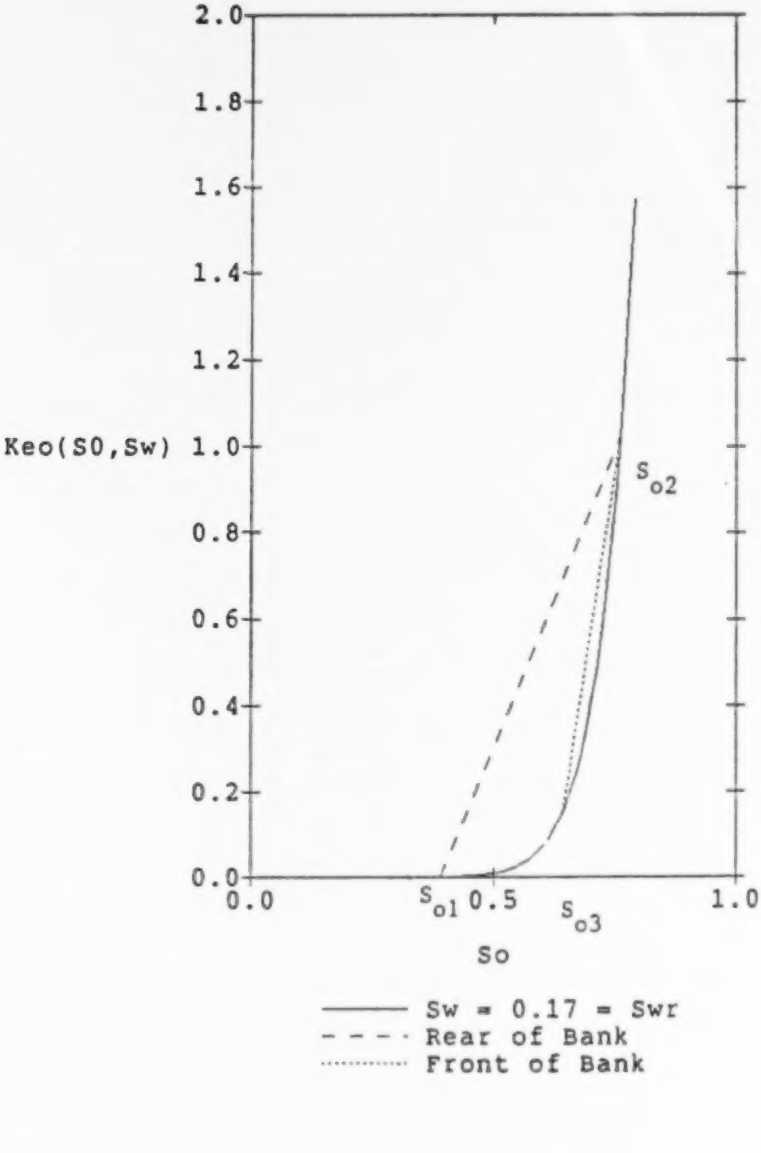

Figure 23: Effective Oil Conductivity and Oil Bank Speeds

balance computations. A volume balance of the oil is then an independent check of the solution. Obviously in a correct solution of a conservative problem, the volume of oil applied must at all times equal the volume of oil in the soil. For all the cases run, only insignificant errors in volume were found. Since this is a necessary condition for the solution to be correct, the correct volume balances prove existence of the solution. Further, it is the unique solution, as the two jump equations which are in effect being solved simultaneously have two unknowns: the speed of the leading edge of the bank, and the oil saturation in the bank S_{o2}. The other oil saturations (S_{o1} and S_{o3}) are determined by the boundary condition of the problem.

The necessity of assuming the existence of the oil bank can be shown as follows. If the discontinuity in oil saturation were neglected, the boundary condition would still specify that S_{o3} is greater than S_{o1}. As the water front invades the region where the oil exists, the oil saturation would drop from S_{o3} to S_{o1}. The total mass, however, is the sum of the oil mass above and below the water front. Above the water front there is less mass than before the water infiltration started, while below the water front there is the same amount of mass as would exist if no water was invading. Thus there would be a net loss of mass caused by the infiltrating water.

A dissolved constituent carried by the fluids is indicated in Figure 21. Here the constituent was hydrophobic and slightly sorbed ($k_o = 200$, $k_s = 10$, $\rho_b = 1.5$). The deeper line labeled ``constituent" (AG) on the figure shows the leading edge of the constituent. Its speed is given by equation 33. The speed is independent of concentration and depends only on the saturations, fluxes, and partitioning relationships. The oil bank causes the speed of the constituent to increase at point C, because the oil flux and saturation are elevated in the bank. When the bank passes (point F), the speed slows in accordance with the oil and water fluxes and saturations behind the bank.

Initially, equilibrium concentrations are established in the soil according to equation 39. When the boundary condition changes, as at time $t = 5$ hr, so does the initial concentration in the soil. A discontinuity in concentration is created that then begins to migrate downward at the concentration velocity (line BD). Above this line the concentration in water is 0.4975, while below it is 0.5000. The small difference in concentration results from the constituent being hydrophobic; most of the constituent resides in the oil. Note that this solution results in near perfect mass balances for the constituent.

Unsteady Oil Banks--

Of course, problems of realistic interest include drying of the profile and the analogous draining of the oil. Once again the increased water saturations due to a rainfall event cause the oil permeabilities to increase. Behind the water front the oil would move faster than if no infiltrating water was present. The abrupt change in oil flux occurring at the location of the water front again must lead to the existence of an oil bank, if mass is to be conserved.

Figure 24 shows a case where oil was applied to the soil for an hour. Later water was applied, also for an hour. Now it is the drainage or unsteady portion of the oil event that is affected by the water. There is again a discontinuity in the oil's domain, driven solely by the water flux. The jump condition can be applied to both edges of the oil bank. In general the conditions for the rear of the bank are

$$\frac{dz_{wf}}{dt} = \frac{dz_{rb}}{dt} = \frac{K_{eo}(S_{o2},S_{w2})-K_{eo}(S_{o1},S_{w1})}{\eta(S_{o2}-S_{o1})} \qquad (56)$$

and the leading edge

$$\frac{dz_{fb}}{dt} = \frac{K_{eo}(S_{o4},S_{w3})-K_{eo}(S_{o3},S_{w3})}{\eta(S_{o4}-S_{o3})} \qquad (57)$$

In this example the water saturation ahead of the water front is at residual ($S_{w2} = S_{w3} = S_{wr}$), where the numeric subscripts on the saturations refer to Figure 25. Since the oil saturations may vary throughout the profile, the various saturations are those immediately adjacent to the jumps (Figure 25). At the water front the oil saturation jumps from S_{o1} to S_{o2}, while at the leading edge of the bank it jumps from S_{o3} down to S_{o4}.

A complication arises in that there are three unknowns: the oil saturations S_{o1}, S_{o2}, and the speed dz_{fb}/dt, while there are two jump equations (S_{o3} depends on S_{o2} and S_{o4} is known from the previous oil drainage pattern). This presents a difficult problem, which has been resolved via numerical experimentation. This work has shown that the only solution that conserves mass is the solution where the water displaces all the mobile oil

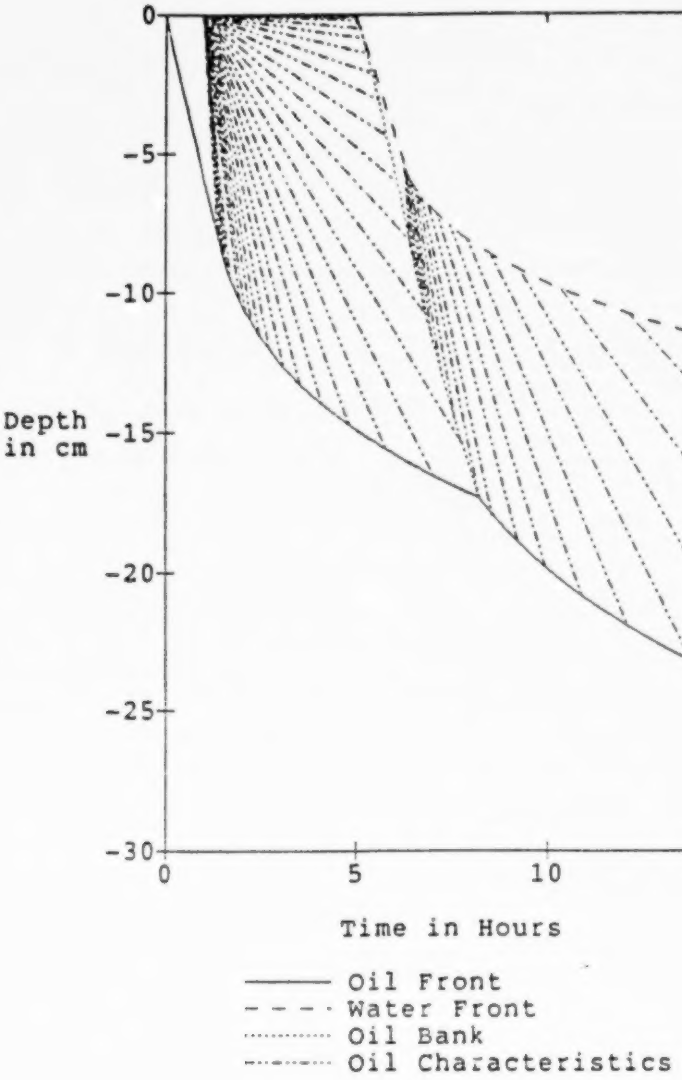

Figure 24: Unsteady Oil and Water Migration

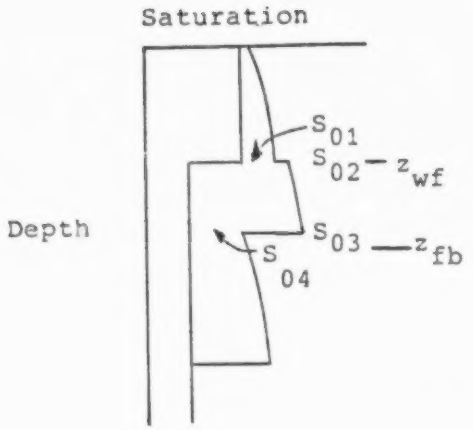

Figure 25: Hypothetical Unsteady Oil Profiles

from behind the front. The oil is left at its residual saturation after the passage of the water (S_{o1} on Figure 25 is always equal to S_{or}). Equation 26 becomes

$$\frac{dz_{wf}}{dt} = \frac{dz_{fb}}{dt} = \frac{K_{eo}(S_{o2},S_{w2})}{\eta(S_{o2}-S_{or})} \tag{58}$$

Here again, existence of a solution requires conservation of the oil volume. In effect, an integral continuity equation, which is applied to the entire profile, is being added to the system of equations that are solved.

The base characteristic plane shown in Figure 24 and the accompanying profiles represent a solution that conserves volume throughout the entire event. The maximum oil volume balance error (computed numerically) was 0.083% at 6 of the 8 solution points between 6.25 and 6.40 hours. Using a code where the water solution was purely analytic, maximum errors of 0.02% were achieved. Thus existence of the solution is proved numerically. Several other proposed solutions which allowed oil drainage behind the water front did not conserve volume, and therefore are not valid solutions. They fail to conserve mass as soon as the water event begins. This is when dz_{rb}/dt is a constant and thus no unsteady water flow is involved. This means that the attempted solutions fail for the simplest case: unsteady flow in the oil only. Since the system has been shown to remain hyperbolic when the water saturation is constant, that these trial solutions fail is not due to the system of equations becoming nonhyperbolic.

The oil bank is driven by the invading water, the speed of which solely determines the bank saturation (in the solution that conserves mass). The water causes the discontinuity in the oil saturation that occurs across the rear of the oil bank. Therefore, the discontinuity is not then, the result of the oil's governing equation, and only exists because of the invading water. The KOPT model shows that where there is no water front, mass is conserved with only a discontinuity at the oil front. The rear of the oil bank is of a different character than the shock that is created due to the nonlinearity of the governing equations (i.e., the oil front).

The bank saturations are determined by finding the saturation, S_{o2}, at which

$$\eta\, C\, S_{o2} - K_{eo}(S_{o2},S_w) = \eta\, C\, S_{or} \equiv f(S_o) \qquad (59)$$

where C is the speed (or celerity) of the water front. The last equation is equation 58 rearranged with $S_{o1} = S_{or}$. This equation has a trivial solution at $S_{o2} = S_{or}$, since $K_{eo}(S_{or},S_w) = 0$. There may also be a solution for the oil bank: $S_o = S_{o2} > S_{or}$. Figure 26 shows values of the function $f(S_o)$ for gasoline in a sandy clay loam soil ($\varepsilon = 8.8$) and various water front speeds. Bisection is used to locate the solution S_{o2} in an interval from the relative maximum of these curves, S_1, to the maximum oil saturation, $S_{o(max)}$. The saturation S_1 is found first by solving

$$\frac{\partial(\eta C S_o - K_{eo}(S_o,S_w))}{\partial S_o} = 0 \qquad (60)$$

which has a relative maximum at

$$\eta\, C = \frac{\partial K_{eo}(S_o,S_w)}{\partial S_o} \qquad (61)$$

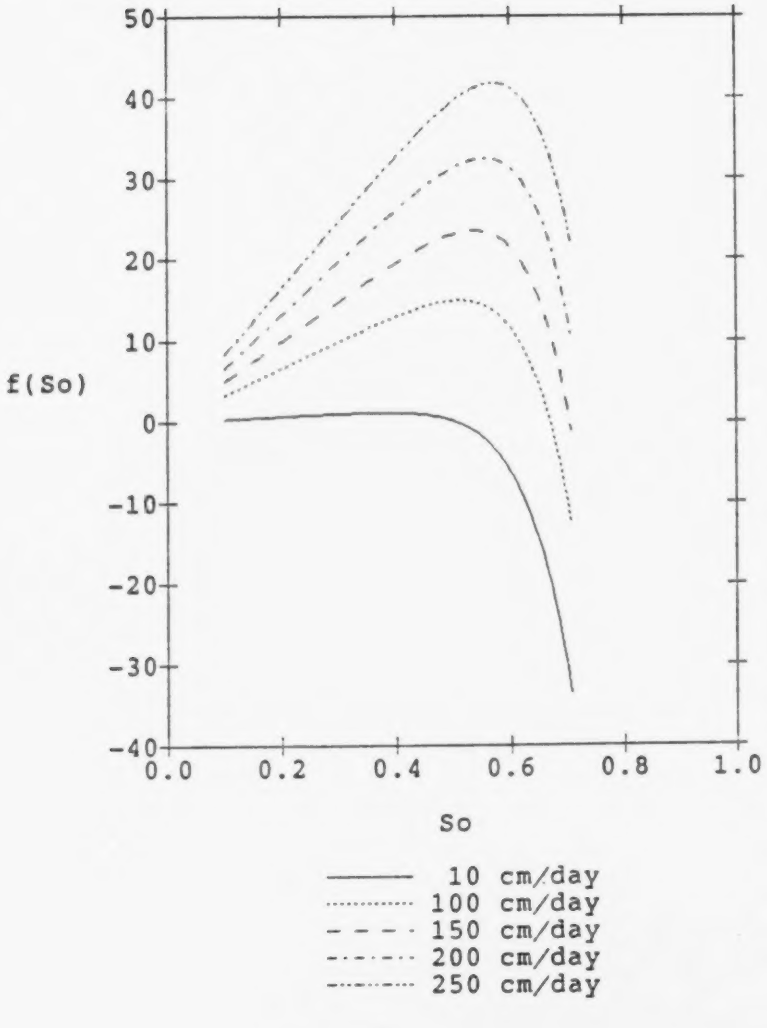

Figure 26: Oil Bank Function

The last equation is solved by bisection over the interval $S_{or} < S_1 < S_{o(max)}$. By locating the relative maximum at S_1 first, S_{o2}, is assured to be in the search interval for the oil bank saturation determination. Since the oil bank function is double valued, this two step procedure is necessary to have a reliable numerical method for determining the oil bank saturation.

The implication of the solution presented in Figure 24 will be discussed subsequently. Most strikingly, all of the mobile oil behind the water front is displaced by the water. This is directly analogous to the steady state case, where the saturation S_{o1} is determined by the surface oil flux. Here, though, the flux is zero and the corresponding oil saturation is S_{or}. In both cases the boundary condition controls the magnitude of the oil saturation immediately behind the water front.

Note that the gross features of this unsteady event are similar to the quasi-steady case. For both there are water and oil fronts and an oil bank driven by the speed of the water front. In the unsteady case, the oil ahead of the bank, as well as that in the bank undergoes drainage. This involves the method of characteristics part of the solution, along with the equation for the fronts, in determining the oil and water distribution.

In contrast to the steady state case, the oil saturation is only constant throughout the bank under restricted conditions. If the saturation S_{o1} and the speed dz_{wf}/dt are constant, then the bank saturation S_{o2} is also constant (see the 6.0 and 6.1 hour profiles on Figure 27). This makes the saturations constant throughout the bank ($S_{o2} = S_{o3}$) as at each point in time of the solution the same saturation is found in the oil bank. As long as the conditions that created the bank remain the same, no mechanism exists for causing a change in saturation in the bank. This occurs in the present case when the water front moves at a constant speed. The solution of the model shows that variable saturations behind the bank, S_{o1}, do not occur. So the constant speed water front always gives a constant oil bank saturation.

Alternatively, variable water front speeds, dz_{wf}/dt, create unsteady oil banks characterized by variable bank saturations ($S_{o2} \neq S_{o3}$). Since the speed of the water front slows as the water undergoes unsteady drainage, the oil saturations in the bank at the location of the water front continuously are reduced. Continuously decreasing oil

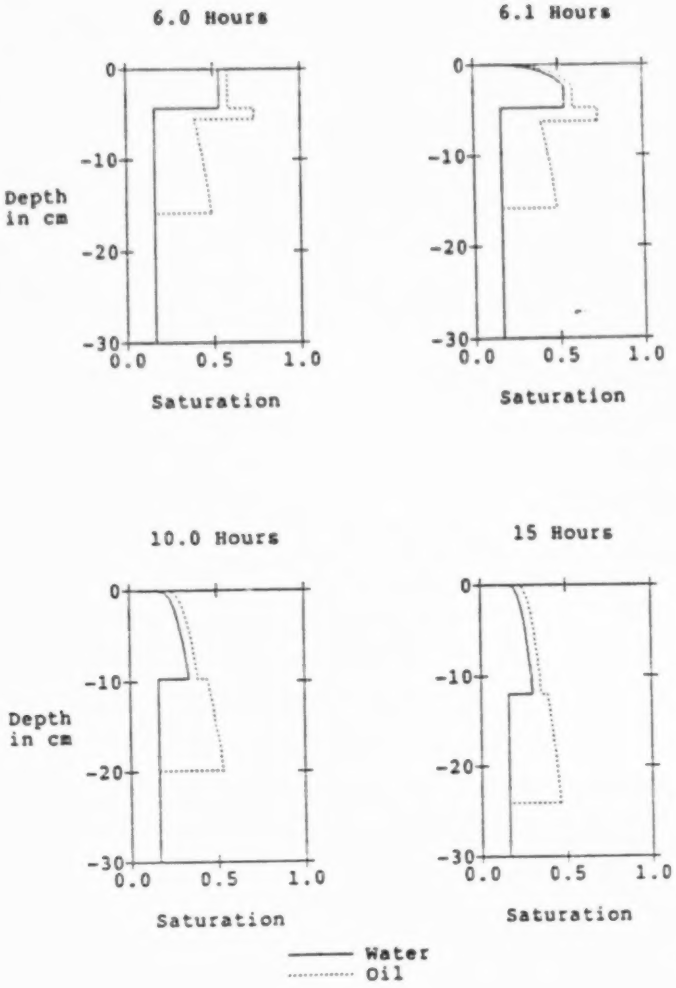

Figure 27: Profiles for Unsteady Flow Example

saturations means that the method of characteristics solution holds. Therefore, oil characteristics must originate along the waterfront.

As time goes on and the water front slows, each characteristic carries lower oil saturations. The simple wave pattern emerges, but is not centered as for an undisturbed drainage pattern. Profiles drawn through the bank during this time show that the bank itself is undergoing drainage, illustrated by the profiles at 10 and 15 hours in Figure 27. In general the bank saturations decrease with time as the oil is spread out at ever lower saturations. Although the immediate effect of the infiltration of water is to increase oil saturations locally (in the bank), the overall effect is to spread the oil out over a region at its residual saturation quicker than the undisturbed drainage would.

Mathematical analyses of shock fronts (which are the analogous counterpart to wetting fronts in gas dynamics) indicate that when characteristics are followed forward in time, they intersect shock fronts (Rozdestvenskii and Janenko, 1980, and Lax, 1973). When they are followed backward in time, they do not intersect shocks. The solution presented above, apparently is in violation of these rules. Oil characteristics originate at the water front; tracing them backward intersects the discontinuity in both oil and water saturations. As discussed above, the rear of the oil bank is not a shock as it results from the change in oil flow domain, caused by the water.

An important consideration, which has not yet been addressed is the mobility ratio (K_{sw}/K_{so}) of the liquids. For highly viscous oils, the maximum conductivity, $K_{eo}(S_{o(max)})$, can easily be less than values that would be required by the invading water. Such cases represent unstable displacements, where the oil cannot be completely displaced by the incoming water. Some amount of mobile oil remains behind the water front. In these cases, ``fingering" occurs as the water displaces some of the oil (Homsy, 1987, and Kueper and Frind, 1988). This indicates that flow of the liquids is no longer kinematic and that pressure gradients are important. The assumption that the water solution is independent breaks down as all the saturations must be determined dynamically.

In Figure 26, the curves for the 200 and 250 cm/day water front speeds have no nontrivial solution in the range of possible oil saturations. This can be seen in the figure, since the solution occurs at the same function value as the $S_o = S_{or}$ end point. For the 250 cm/day speed the function value at $S_{o(max)}$, 22.094, is above the endpoint value, 8.200. At this speed, then there is no value of the oil saturation that satisfies the jump conditions, and the kinematic model breaks down. The simulation ceases and the message ``Unstable displacement--model terminated" is output. The factors which control this condition are the density and viscosity of the oil, the speed of the water front, and the pore size distribution of the soil. A proposed method to extend the kinematic model to cases where the oil banks cannot form under kinematic conditions is discussed in Weaver (1988).

KROPT Model Results

Example 4 Oil Spill in Coarse Sand--

The first 80 hours of the base characteristic plane for an oil spill is shown in Figure 28. No characteristics are drawn in the figure, but they exist in all of the oil banks and the original drainage region. The input parameters can be found in Table 5. This example is similar to the unsteady oil bank example, but is meant to illustrate the effect of multiple rainfalls on the oil. Each rainfall that passes the rainfall event that is driving the oil bank, causes the water front speed to increase (points A and B on Figure 30). Each time this occurs a new oil bank is created, due to the abrupt increase in water front speed, and corresponding jump in oil saturation (lines AD and BE). Since the banks move faster than the oil front, they surpass the oil front, causing its speed to increase (points C, D and E).

Four oil profiles are shown in Figure 29. By 11 hours after the beginning of the oil spill, the first rainfall has created the first of the oil banks, with a constant saturation of 0.8195. The original undisturbed oil drainage profile is below the bank. At 46 hours this bank has long since passed the original oil front and replaced it. The second rainfall has begun and reached a depth of 14 cm. By 56 hours the second rainfall has passed the first, triggering a new oil bank. The water front speed slows continuously from point A on, so the second oil bank contains ever decreasing oil saturations. By 72 hours the third rainfall has passed the second, triggering the third oil bank.

The entire simulation of 180 hours is shown in Figure 30. The last rainfall (line EF) is of such a great magnitude, that it drives a very narrow oil bank ahead of it (Figure 31). After 137.9 hours the rainfall is spread out over 457.4 cm at its residual saturation of 0.05. The maximum oil volume balance error for the oil +0.29%, while the maximum error for water is +0.09%.

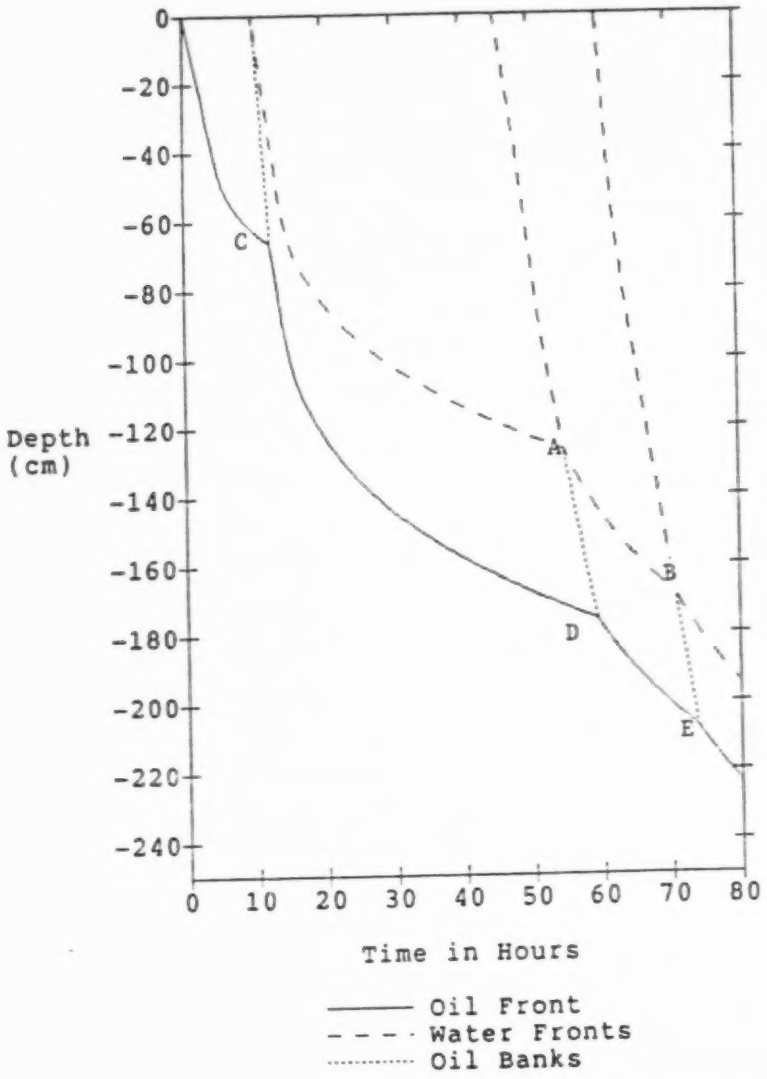

Figure 28: Example 4 - Base Characteristic Plane

Table 5: Examples 4, 5, and 6 Input Data

		Example 4	Example 5	Example 6
Soil (a)		Coarse Sand	Sandy Clay Loam	Sandy Clay Loam
K_{vs}	cm/day	720.0	118.5	118.5 (a)
λ		0.550	0.3446	0.3446 (a)
n		0.349	0.328	0.3900 (a)
ρ_b	gr/cm^3	1.72	1.70	1.61 (b)
f_{oc}	%	n/a	1	1
Water				
S_{wr}		0.0500	0.2287	0.2041 (b)
S_w(t=0)		0.2000	0.4000	0.4240 (b)
u_w	gr/cm/day	872	872	872
Oil				
u	gr/cm/day	1285	471	1000 (c)
ρ	gr/cm^3	0.73	0.65	0.65 (b)
S_{or}		0.05	0.10	0.10 (d)
half life	days		(c)	360 (d)
lag time	days			
loading	cm/day	2.0	6.0	
time	days	0.167	5.0	
volume	cm^3/cm^2			0.3597 (b)
depth	cm			15.2 (b)
Constituent				Toluene, Pyrene
C_o (init)	mg/l		200	396, 1669 (b)
half life	days			n/a, 35 (b)
lag time	days			
k_o			240 (b)	240, 2089 (b)
k_h			0.10 (b)	0.10, 0.0 (b)
k_{oc}			60 (b)	60, 60 (b)
Climate				
Temperature	°C	25	20	21.4 (b)
Evaporation	cm/day			0.1543 (b)
Relative Humidity		0.61	0.32	0.5 (d)

a) soil data from Brakensiek et al., 1981
b) from Ryan et al., 1987
c) see text
d) value estimated for example 6
e) potential evaporation rates calculated from Austin, TX climatic data

Example 4	Rainfalls Intensity cm/hr	Beginning hr	Ending hr
1.	2.5	10.0	13.0
2.	1.5	45.0	49.0
3.	3.5	60.0	61.0
4.	2.0	100.0	104.0
5.	6.0	130.0	135.0
6.	1.0	150.0	152.0

	Intensity cm/day	Beginning day	Ending day
Example 5			
1.	18.0	9.0	9.3
2.	5.0	15.5	15.7
3.	30.0	20.0	20.1
4.	30.0	40.5	40.6
5.	5.0	52.0	52.1
Example 6			
a) soil column comparison			
1.	16.0	57.0	57.3
2.	18.0	90.0	90.3
3.	18.0	119.0	119.3
4.	18.0	151.0	151.3
5.	18.0	183.0	183.3
6.	18.0	202.0	202.3

b) Randomly generated rainfalls for Austin, Tx
See figure 4.34 for rainfall sequence.

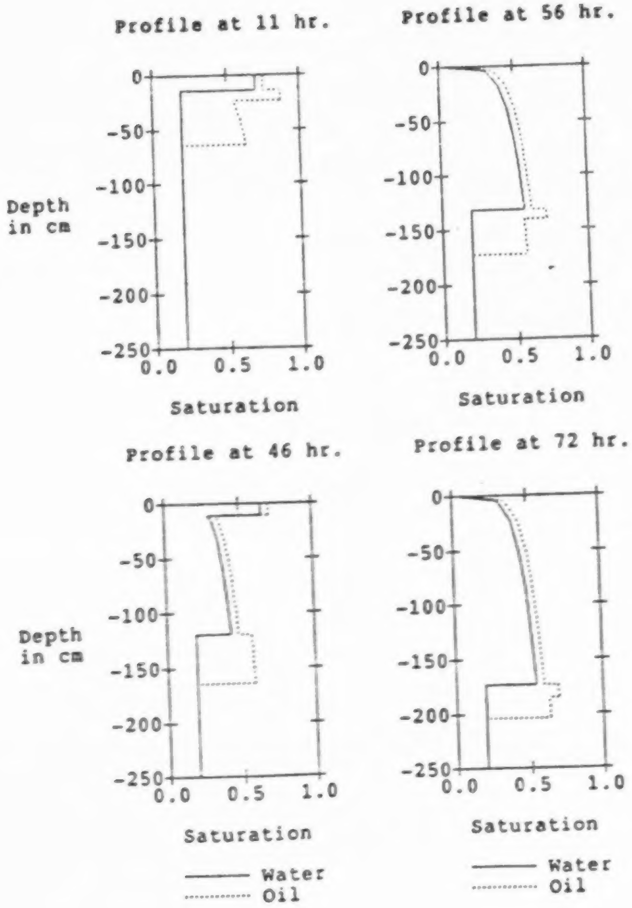

Figure 29: Example 4 - Profiles at 11, 46, 56, & 72 Hours

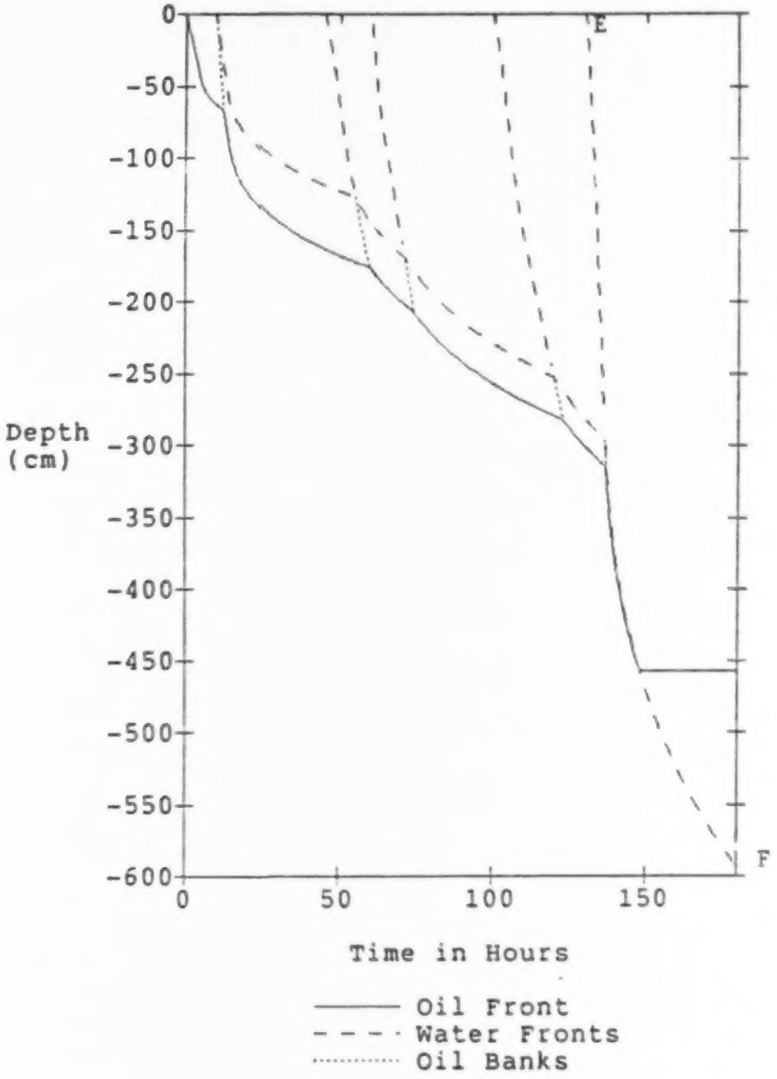

Figure 30: Example 4 - Base Characteristic Plane (continued)

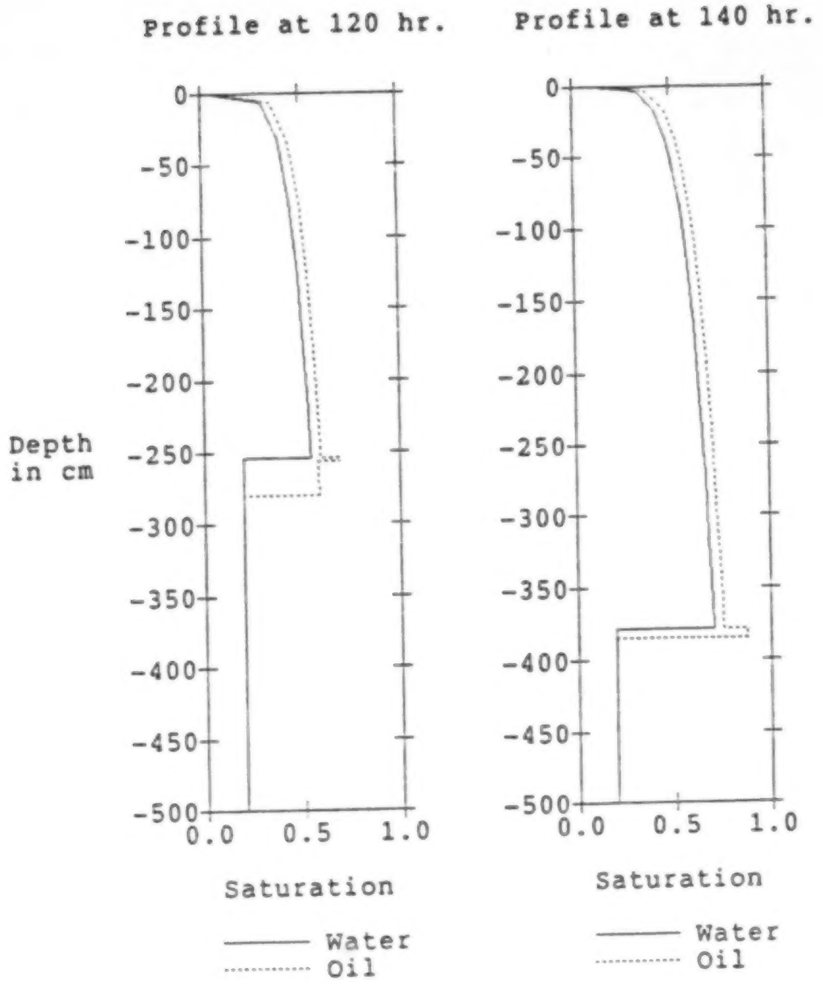

Figure 31: Example 4 - Profiles at 120 and 140 Hours

In cases like this one, where a relatively small volume of oil is released, a series of rainfall events may cause the oil to be immobilized over the depth given by equation 52. In the kinematic model with no rainfalls, the oil will only be immobilized after an infinite amount of time. The rainfalls may greatly reduce the time required for immobilization; 137.9 hours in this case.

Saturation histories for 50, 100 and 200 cm are presented in Figure 32. At 50 cm the first two oil banks are visible as an abrupt increase in oil saturation. Once the rainfall events pass the history depth, the oil is left at its residual saturation for the remainder of the simulation. The rainfalls can be seen at the deeper depths also and corresponding events are marked on the 3 histories.

Example 5: Gasoline Leak into Sandy Clay Loam--

The next example is of a gasoline leak into a sandy clay loam soil (Table 5 and Figures 33 through 36). The soil in this example is of a wider pore size distribution than the sand in example 4, as indicated by the Brooks and Cory exponents - 6.6 for the sand and 8.8 for the sandy clay loam. The water relative permeability curve for this example is given in Figure 33. In this type of media the relative permeability drops very rapidly once the saturation drops. After a rainfall event in such soil, drainage will appear to cease at relatively high water saturations, because the relative permeability is so low. This phenomena is responsible for the poorly defined concept of field capacity, which is defined as the moisture content after gravity drainage has ceased. (The kinematic model, of course, shows that gravity drainage never truly ceases.) In example 5 the influence of soil type appears as relatively slowly moving fronts, with high saturations.

Figure 34 shows a 60 day simulation for infinite (nondegrading) and 360 day gasoline half lives. Three of the rainfalls are intense enough to create oil banks (those beginning at points A, C, and D), while others (points B, E, and F) remain behind the deepest water front. The gasoline is more mobile ($K_{so} > K_{sw}$) so that it is difficult for the water to go deep enough to bypass the gasoline. The gasoline can move as fast as required by the water, in this case. (The possibility of unstable displacement remains, since the initial infiltration capacity of the soil is infinite).

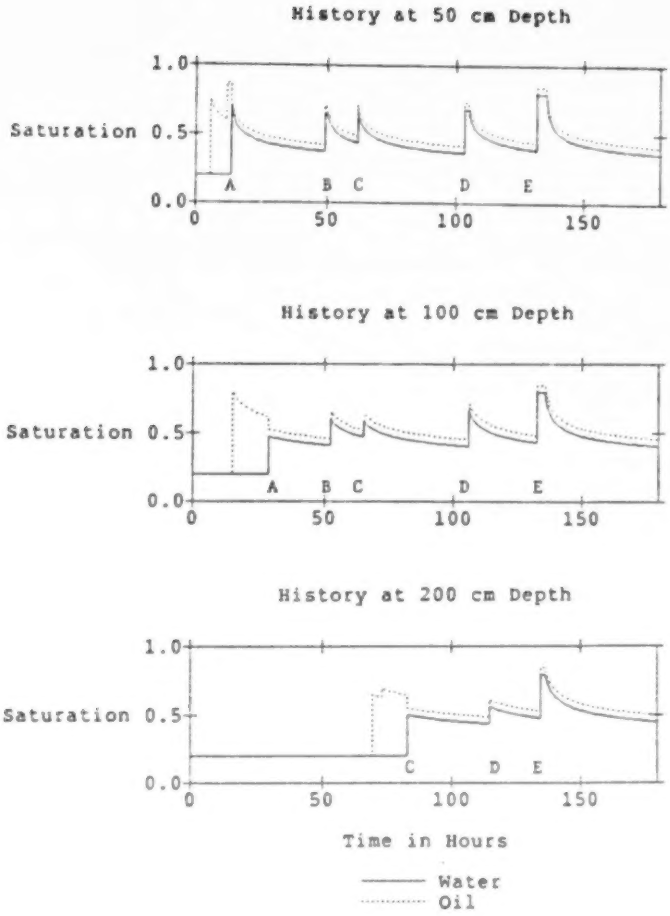

Figure 32: Example 4 - Histories at 50, 100, and 200 cm Depths

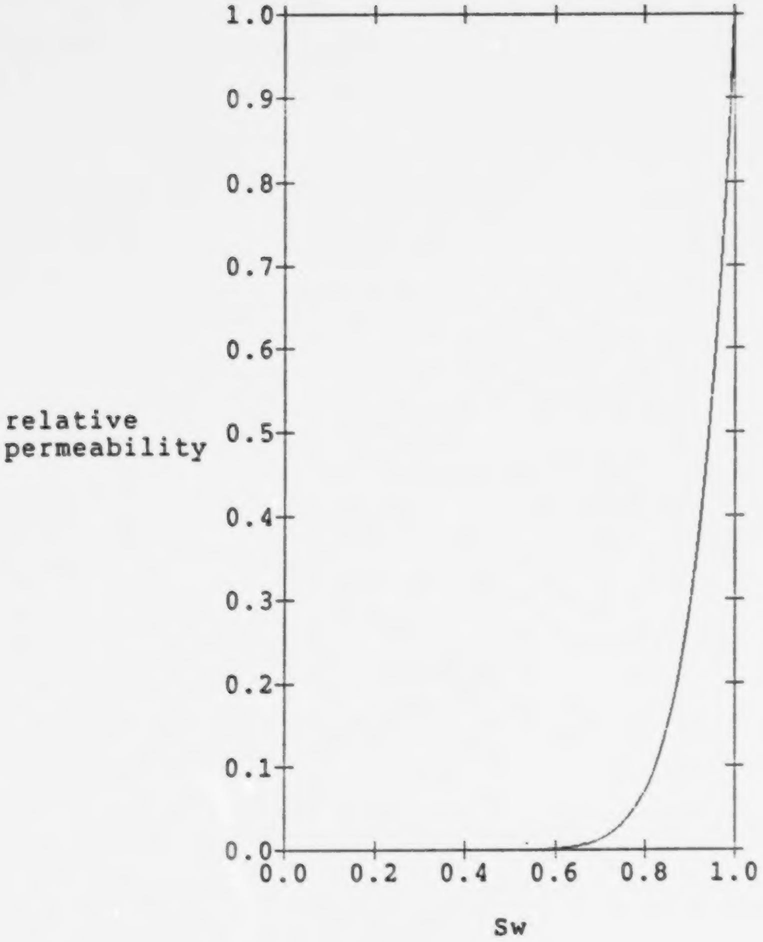

Figure 33: Water Relative Permeability in a Sandy Clay Loam Soil

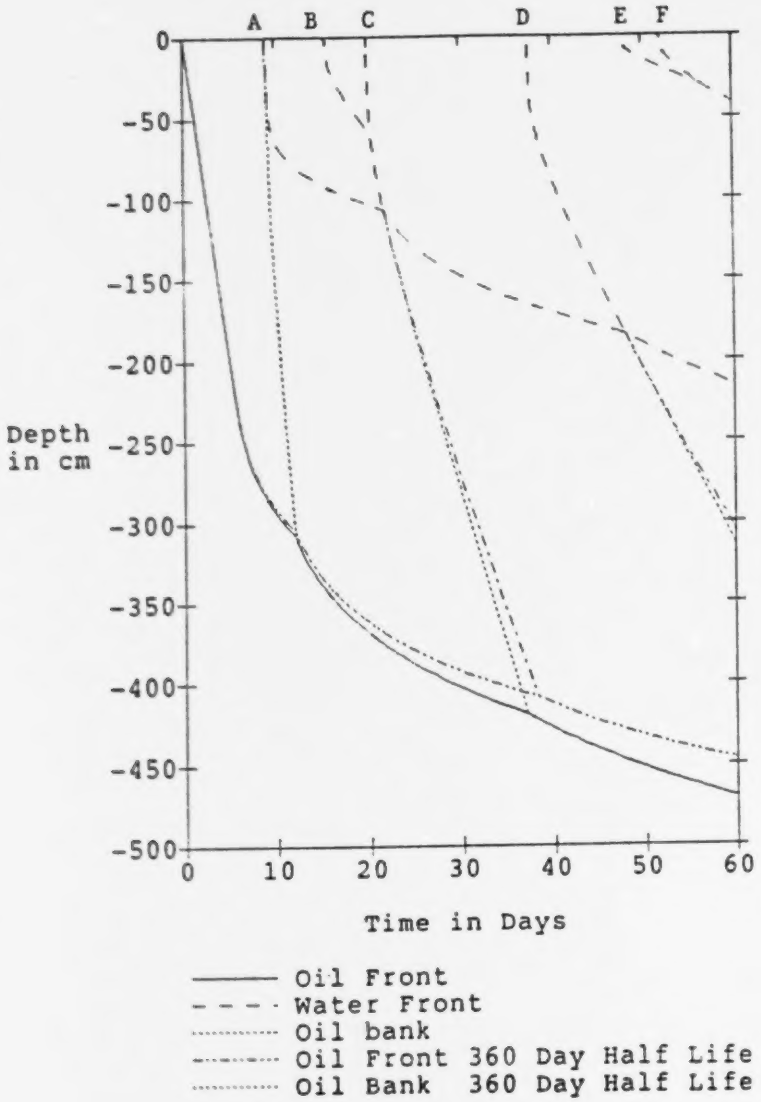

Figure 34: Example 5 - Base Characteristic Plane

Oil profiles shown in Figure 35 also reflect the high mobility of the gasoline, because the oil saturations in the banks are lower than the water saturation in the fronts driving them. The oil saturation jumps are of such a low magnitude that for all practical purposes they are undetectable. The jumps are needed, however, to maintain the accuracy of the computation. Somewhat unexpectedly, the oil banks persist over long periods of time. The relative permeability function leads to low effective hydraulic conductivities as the oil saturations become reduced as the banks move away from the water front. The slowness of the banks means that more than one bank may be present at any given time. As a result of this example, the code has been modified for this possibility.

When the oil decays, the features of the solution move slower as time goes on. The reduction in effective hydraulic conductivity is evident in both Figures 34 and 35. The profiles show decreased extents of gasoline, with small reductions in gasoline saturation. Another feature, visible in the 40 and 60 day oil profiles, is that the water front always leaves the oil at its residual saturation at the water front. This oil then degrades, so its saturation is reduced further. In contrast to example 1, the locus of points at residual saturation is defined mainly by the water front.

The extent of a dissolved constituent, with the properties of toluene (Ryan et al., 1987) is indicated in Figure 36. The leading edge of the constituent generally mimics the oil front, but is retarded due primarily to sorption. Only a small amount of this material volatilizes. Concentration profiles are found in Figure 37a, and show increasing concentration with time, due to oil biodegradation. For comparison, Figure 37b shows profiles for the same initial concentration in gasoline of a constituent with benzene's partitioning properties ($k_o = 134$, $k_h = 0.15$, $k_s = 6.0$). The partitioning relationship (equation 39) gives higher water concentrations for the benzene since it is less hydrophobic than toluene. As a result the toluene can migrate deeper that the benzene, since it is carried with the faster moving oil.

The examples presented above illustrate the fluid's migration where the initial water saturation is a constant. The equations for oil migration reduce to equation 21, since $\partial S_w/\partial z$ and λ_o are equal to zero. An attempt was made to simulate a case where there was an initially uniform water profile in the soil, that began to evaporate before the oil was released. Since $\partial S_w/\partial t$ is not now equal to zero, the oil saturations vary along the characteristics, curving even when λ_o is zero. Once out in front of the variable water profile the oil characteristics become straight lines.

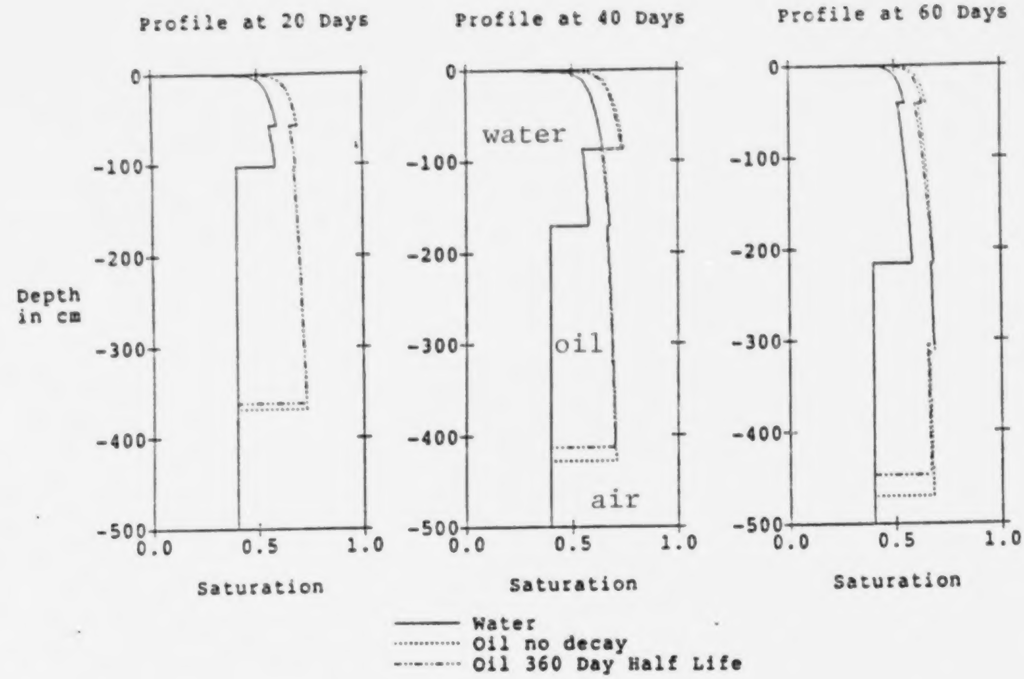

Figure 35: Example 5 - Profiles at 20, 40, and 60 Days

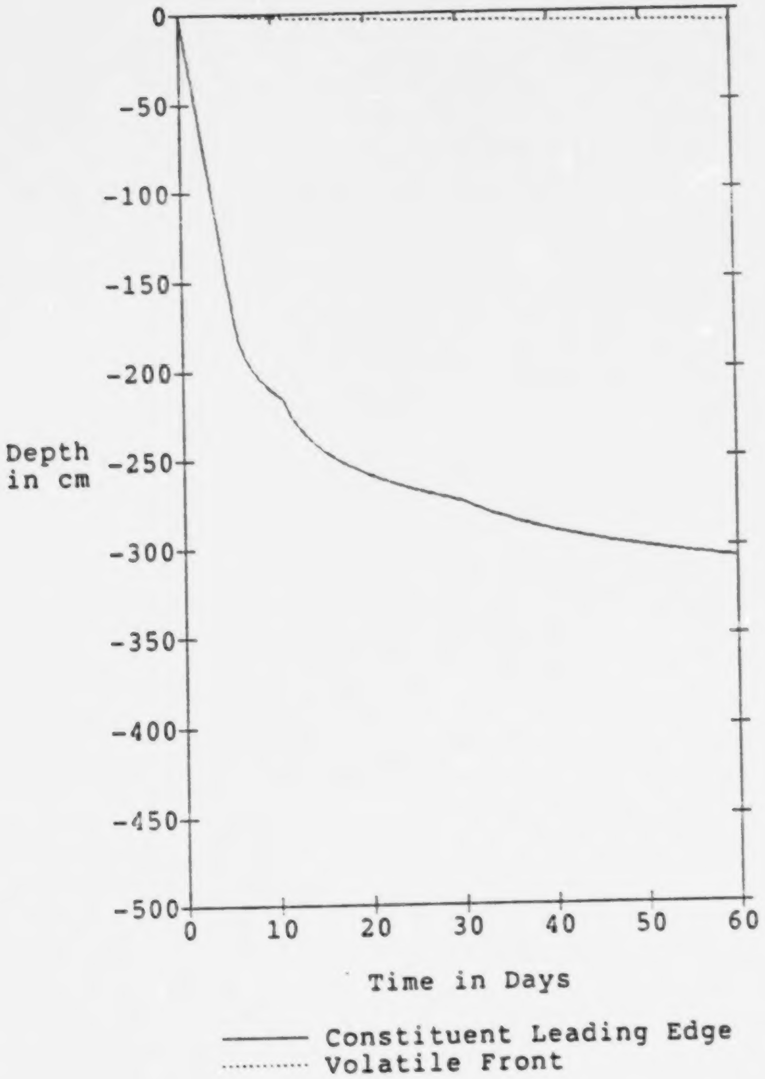

Figure 36: Example 5 - Constituent Distribution

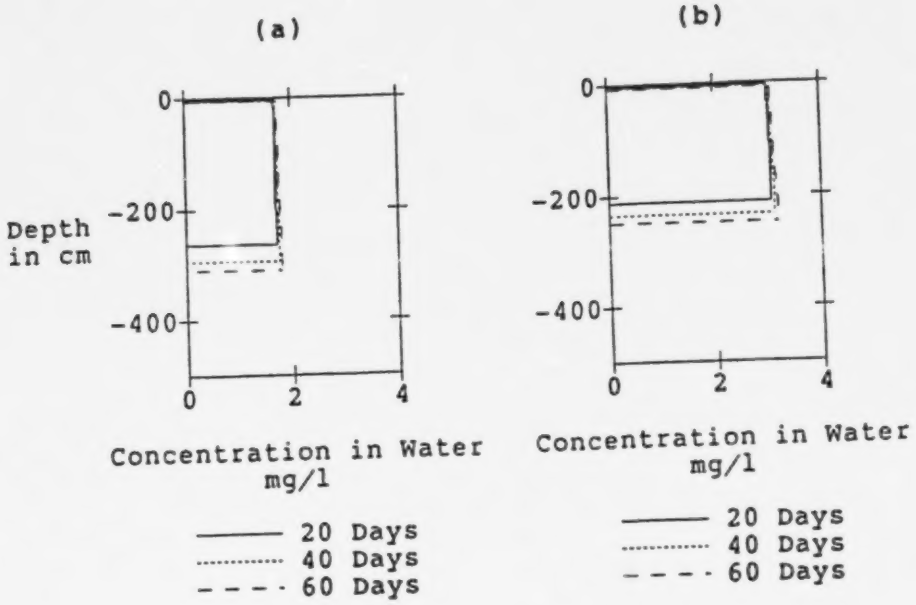

Figure 37: Example 5 - Concentration Profiles, (a) toluene and (b) benzene

This presents some extreme difficulties for the model. First, the water profile has an infinite slope at the ground surface. This causes a problem for the oil characteristics that originate at the surface during the oil release. They face an infinitely large decrease in saturation, resulting from equation 20, in an infinitesimally small depth. The RKF1(2) solver uses function evaluations at the surface, and two depths for the first time step (for each characteristic). Error must be introduced into the solution to avoid the saturations becoming large negative numbers as the solution starts. In a fine sand the error was approximately 5%, while in a silty sand the error was about 50%. For this reason this case was not pursued any further.

When water enters a soil containing variable water saturations, the water front speed increases at first, since the water saturations ahead of the front increases. In this case, the oil bank saturations increase as time goes on, instead of remaining the same or decreasing as in the previous examples. The speed of each emerging oil characteristic is higher than that of the previous characteristic. The characteristics could cross, creating a new discontinuity of some type. It was found, however, that the $\partial K_{eo}/\partial S_w$ term in equation 20 acts in such a way to reduce saturations so that the characteristics do not cross.

Variable water saturations make the solution very complicated from the point of view of managing the characteristics. Not only must the curving characteristics be accounted for, but also the equations for the changing oil saturations. There may be several sets of characteristics, associated with different oil banks. In the face of the complexity of the solution, using finite difference techniques for the solution of the characteristic equations appear to be an attractive alternative. Little efficiency would be lost, since the calculation of the characteristics is no longer insignificant.

Example 6 Land Treatment--

Before presenting the land treatment example, some features of the KROPT code specifically designed for land treatment will be discussed. Because of the unresolved limitations of the kinematic model, the land treatment features of the model were built around an immobile oil phase. Oil applied at saturations slightly above residual will not move very far (see example 3 and equation 52). The oil's low flux contributes little to the constituent migration. For a land treatment case the oil, constituent and applied water are incorporated over some depth (the plow zone) into the soil. Multiple waste loadings, irrigation to a specified moisture content and cultivation are capabilities of the model.

The KROPT model requires the initial concentration in oil to be input. This can be calculated from the concentration in the waste according to the mass balance

$$C_{waste} V_{waste} = C_o (V_o + V_w/k_o) \quad . \tag{62}$$

This implies that

$$C_o = C_{o(surface)} = \frac{C_{waste} V_{waste}}{V_o + V_w/k_o} \quad . \tag{63}$$

$C_{o(surface)}$ is then used as input in equation 40 to give the initial concentration in the oil.

Cultivation is expected to occur at a frequency of about 7 days, weather permitting. If no rainfalls are occurring and the average soil moisture in the plow zone is below a specified value, the water, oil and constituent in the plow zone are mixed over the depth. If the moisture content is below a specified value, typically 80% of field capacity, water is added during cultivation. The constituent concentration is now discontinuous at the depth equal to the depth of the plow zone. This creates a problem for the constituent solution as follows. No constituent characteristics are ever lost in the solution, except through volatilization. As more cultivations are performed more characteristics must be created to account for the discontinuities. Only a limited number of characteristics is available in the simulation, though. Even if only one characteristic were used for each discontinuity, after a few cultivations there would not be enough characteristics to continue adding more. The same interpolation problems encountered in applying the evaporation correction would be encountered here, but would be worse since more discontinuities would exist.

This problem was solved by averaging the constituent concentration below the plow zone and assigning the average concentration to the characteristics, each time the plow zone is cultivated. Although the concentrations are in reality not averaged below the plow zone, this is justified by recognizing that the model approximates the transport as advective only and that discontinuities in concentration are smeared by diffusive forces. Also, in this model the motion of the constituent is independent of concentration. Averaging the concentrations does not alter the speeds or arrival times at various depths.

Both averagings use the integral of the constituent mass

$$M_z = \int_0^z \eta \, C \, B(S_o,S_w) \, dz \tag{64}$$

where M_z is the mass of constituent between the surface and depth z. Defining the average concentration, C_{avg}, such that the mass in the profile remains the same gives,

$$M_z = C_{avg} \int_0^z \eta \, B(S_o,S_w) \, dz \tag{65}$$

The last equation is used to find C_{avg}.

The land treatment example is based on soil column experiments performed by Ryan et al. (1987). Input data is found in Table 5. Since the experiments were not designed with the KROPT model in mind, some of the input parameters must be estimated (indicated in Table 5). The experiments were run for 6 months, at the end of which time the columns were destructively sampled for a variety of waste constituents. Toluene and pyrene were selected for comparison of the experiments with the KROPT model. The columns were cultivated every two weeks and checked to assure proper moisture content (80% field capacity → $S_w = 0.4240$). Approximately 5 centimeters per month of water was added to the columns to simulate rainfall. The waste was composed of 18.9% oil and grease, 66.6% water, and 14.5% solids by weight. The effect of the solids was neglected in the model. The column simulated had a waste loading that was 8% by weight of the total of soil and waste.

The experimental results showed no migration of any constituent out of the bottom of the plow zone; except for a few measurements judged anomalous by Ryan et al. (1987). This is close to the result shown in Figure 38 for the soil columns. The toluene and pyrene migrate a small distance (approximately 3 cm over 6 months), because of the high water fluxes from individual rainfall events. The result is due to the constituents being preferentially partitioned to the immobile oil and the low overall water flux. The jumps visible in the leading edge are associated with the arrival of an intense rainfall. The simulated mass balance of the water is shown in Figure 39. A series of rainfalls approximated the times, fluxes and volumes of water added in the experiment. Less water was added for irrigation in the simulation, than in the experiment.

Figure 40 shows the loss of pyrene and toluene from the columns with time. Virtually complete removal is achieved, while the experimental results indicate 85% removal of pyrene and removal of toluene to below the detection limit. Since pyrene is modeled as a nonvolatile constituent, its loss is due solely to its biodegradation half life; the average measured by Ryan et al. (1987) of 35 days was used in the simulation. Toluene, in contrast is lost only through volatilization. The top of the volatile front is indicated in Figure 38. At each cultivation the volatile front is brought back to the surface, causing the rate volatilization to increase temporarily. In the model, irrigation and cultivation occur at the same frequency (14 days), unlike the experiment.

Simulation of the same loading of waste and toluene was performed for a series of rainfall events generated by the methods of Charbeneau et al. (1988) for Austin, Texas

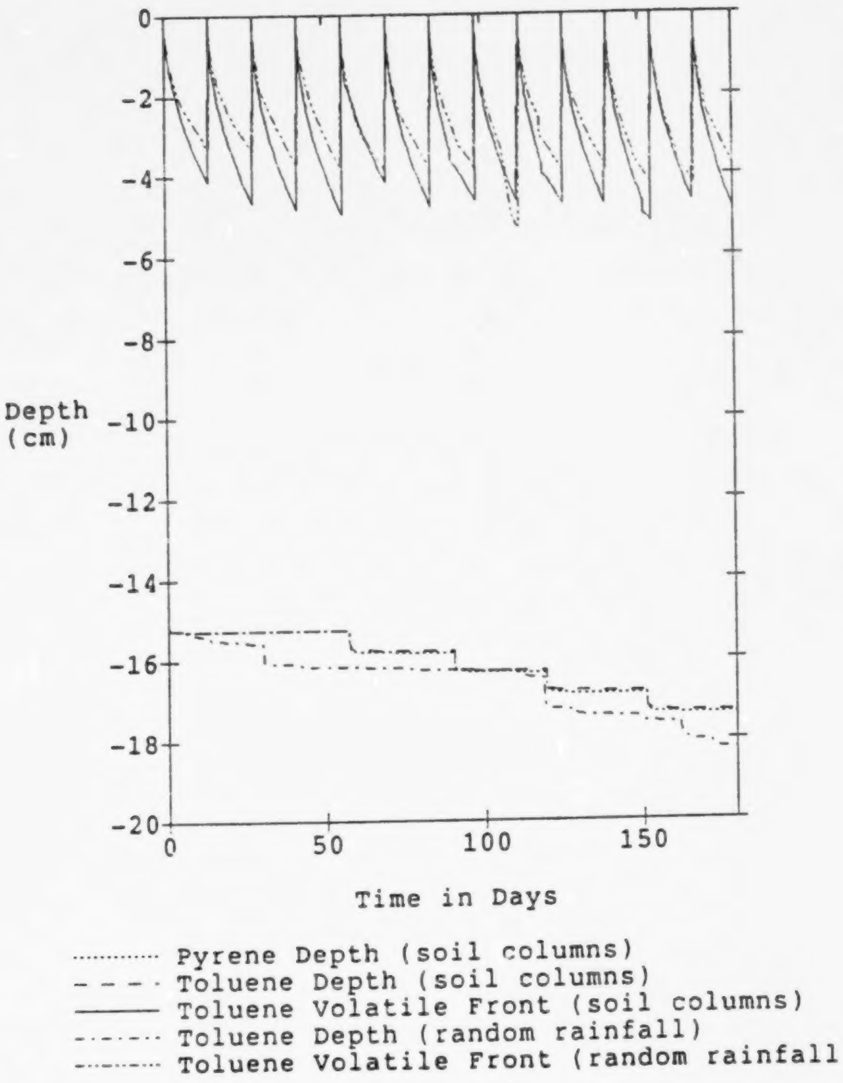

Figure 38: Example 6 - Base Characteristic Plane

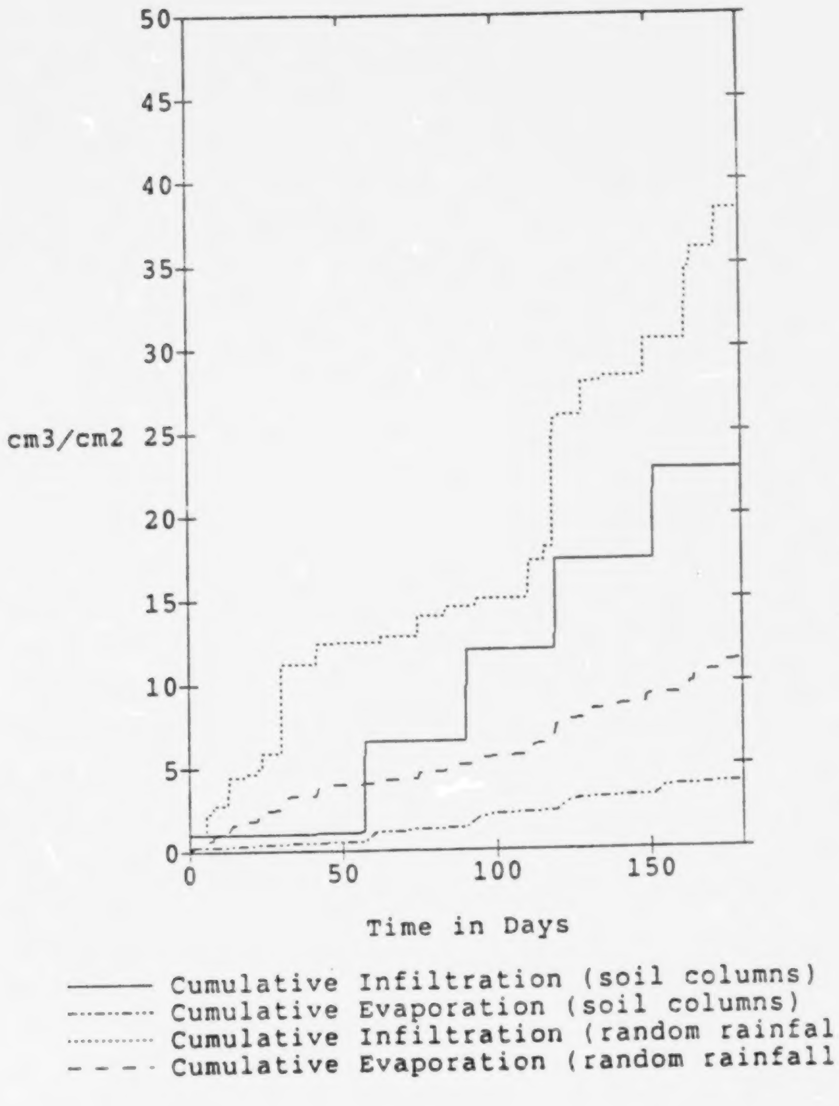

Figure 39: Example 6 - Water Balance

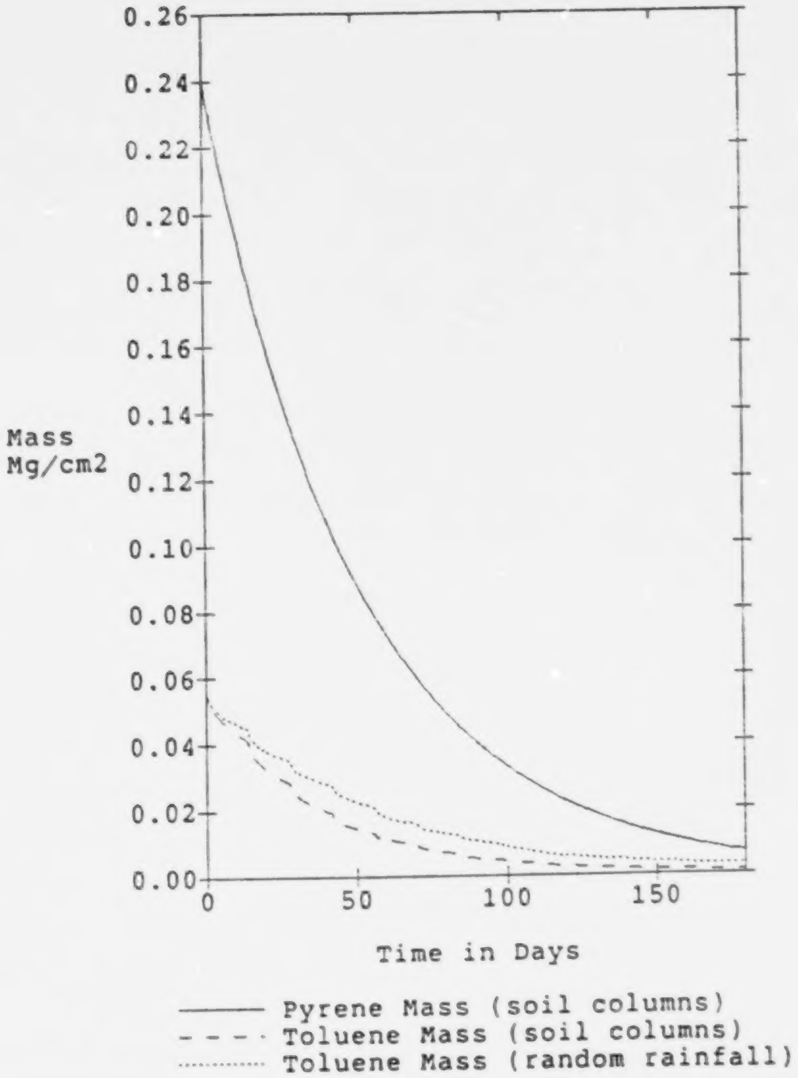

Figure 40: Example 6 - Constituent Mass

climatic conditions. Similar results were obtained for the depth of the toluene determined in the soil column simulation. More water, however, was added to the profile by the random rainfall generation, suggesting that the transport of hydrophobic constituents is relatively insensitive to the rainfalls.

KROPT Model Implementation

The implementation of the full solution in the KROPT code is much more difficult than for the simplified KOPT model. The following features must be included in KROPT,

- for water:
    - solution of the water equation for multiple rainfall events,
    - evaporation of the current rainfall,
    - Green-Ampt flow of the water during the rain,

- for oil:
    - creation of the oil banks,
    - motion of the oil banks,

- for the constituent:
    - biodegradation of oil with varying water saturations,
    - volatilization with variable evaporation rates,

- for land treatment cases:
    - irrigation of the land treatment site for maintaining minimum moisture content,
    - cultivation of the site, and
    - multiple waste loadings at specified intervals.

Table 6 contains a synopsis of the programming details used in the KROPT code, for each of the above items. Included are the number of fronts and characteristics used in the program and the treatment in the controller routine. Since more characteristics are needed than for the KOPT model, more attention must be paid to the data structures. The

Table 6: KROPT Programming Synopsis

Equation	Fronts	Characteritstics	Notes
Water	30	0	Maximum
Oil			
Nondecaying	1	0	Up to 51 characteristic origins saved per bank
Decaying	1	51	10 characteristics used during oil release 41 characteristics used for simple wave
Oil bank	1	51/bank	Maximum characteristics used per bank
Constituent			
nonvolatile	0	11(22)	22 Characteristics for Land Treatment
volatile	1	11(22)	Front is for the volatilization model

Item	Controller Checks	Notes
Water	Beginning of Event	
	End of Event	
	End of $S_{w(max)}$	
	Water fronts passing each other	
	Irrigation at specified frequency	Land treatment sites
	Cultivation at specified frequency	Land treatment sites
Oil	Beginning of Event	
	End of Event	
	End of $S_{o(max)}$	See Figure 4.1, point B
	At least 5 steps through release	Nondecaying oil
	Starting time of each characteristic	Decaying oil
	Oil bank creation	
	Oil bank overtaking oil front	
	Water front overtaking oil front	
	Multiple waste applications	Land treatment sites
Constituent	Characteristic passes oil front	
	Volatilization of entire mass of const.	Remove all constituent equations
Simulation		
	Place solution on even time step	
	Simulation Ending time	
	Profile times	

underlying philosophy in this implementation is to store only the data that must be used again during a time step, and as in KOPT, to store data only for one time step.

The solution algorithm proceeds through the following order: water, oil and then constituent equations are evaluated. Figure 6 shows the subroutines used in obtaining the function evaluations for each partial step taken by the RKF solver (boxes A, B and C of Figure 6). Next to each subroutine is a description of the operations performed in it. The controller structure is also indicated in the figure.

Integration of the profile is done in KROPT by breaking up the profile into intervals and using the Gaussian quadrature routine to integrate each interval of the profile. The breaks are picked so that each discontinuity (oil front, oil banks, water fronts, leading and trailing edges of the constituent) fall on the end points of an interval. An advantage of the quadrature routine is that the function is not evaluated at the endpoints of the intervals, which is where the saturations and concentrations are double valued. A result of this procedure is that the number of function evaluations for the profile varies throughout the solution. The accuracy of the mass balance computation varies, then, throughout the solution. Some cases were found to have errors that, in reality, resulted from the profile integration instead of error in the solution.

COMPUTATIONAL PERFORMANCE

A summary of the code performance is presented in Table 7 for examples 1 through 6. In the first column is the example number and the duration of the simulation, whatever time unit used. Information concerning the RKF1(2) solver steps taken is indicative of the computational effort needed to obtain the solution. In columns 2 through 5 are tabulated the total number of steps taken, the percentage of steps that were rejected, the average number of function evaluations per step, and the average number of model equations used for each evaluation. The CPU time in seconds is reported in column 6 and the time per RKF step in column 7. The runs were made on a Microvax II. Each time listed is the average of three runs made when there were no other users and includes all processing and the I/O. Mass balance computations were performed for each accepted step of the solution, adding, not insignificantly, to the computational burden.

Table 7: Solution Performance for Examples 1 - 6

Example Duration (a)	RKF1(2) Steps				CPU time in sec		Notes (b)
	Number	Percent Rejected	Evaluations/ Step	Equations/ Evaluation	Total	Time/ Step	
1a (180)	212	4.46	2.13	1.00	6.70	0.0316	nd,nc
1b (180)	251	4.38	2.13	30.40	12.86	0.0512	d,nc
2a (545) (c)	294	12.25	2.26	1.00	9.74	0.0331	nd,nc
2b (545) (c)	338	11.83	2.39	12.00	26.16	0.0774	nd,c
2c (545) (c)	383	11.23	2.38	8.72	25.48	0.0665	nd,vc
2d (545) (c)	367	9.26	2.28	32.86	24.73	0.0674	d,nc
2e (545)	382	9.42	2.28	44.26	44.02	0.1152	d,c
2f (545)	411	9.08	2.27	39.98	42.06	0.1023	d,vc
3 (730)	870	7.36	2.23	30.70	80.45	0.0925	d,vc
4 (180)	655	10.38	2.36	3.53	83.89	0.1281	nd,nc
5a (60)	561	7.13	2.25	3.03	78.02	0.1391	nd,nc
5b (60) (c)	639	10.95	2.40	13.54	131.10	0.2052	nd,c
5c (60) (c)	788	11.68	2.42	15.75	164.87	0.2092	nd,vc
5d (60) (c)	835	11.49	2.41	75.74	154.26	0.1847	d,nc
5e (60) (c)	836	11.96	2.43	89.18	202.52	0.2422	d,c
5f (60)	914						d,vc
6a (210)	836	10.05	2.34	25.33	131.59	0.1574	c
6b (210)	1757	4.89	2.16	26.46	275.27	0.1567	vc
6c (210)	4239	8.82	2.30	27.25	538.13	0.1269	vc,rr

(a) duration of simulation in whatever time unit used

(b) abbreviations: c, with nonvolatile constituent; d, decaying oil; nc, with no constituent; nd, nondecaying oil; rr randomly generated rainfall events; vc, with volatile constituent

(c) results not presented in the text

Example 2 was selected for a comparison of various KOPT model simulations. The first three (2a - 2c) have nondecaying oil and thus the fewest number of equations to solve. For a nondegrading oil with no dissolved constituent exactly 1 equation is solved per step. Fairly large steps were taken, which required a high percentage of the steps to be rejected. The dissolved constituent adds exactly 11 equations to the simulation (example 2b). Smaller steps were taken in order to satisfy the truncation error criteria on all 12 equations. When the constituent is volatile (2c) another equation is added for the volatilization model. The average number of model equations is lower than in case (2b), since all of the constituent is volatilized before the end of the simulation. When the oil is degradable (2d), the number of equations jumps, because the characteristic equations are solved to find the characteristic locations. The average number is less than the total allowed (51), because some characteristics are dropped from the solution set as time goes on. The number of steps increases, again for the reason that more equations must not exceed the truncation error criteria. The same trend continues when the dissolved constituent is added (2e and 2f). The CPU times for these cases increase as expected as the complexity of the simulation increases.

A similar comparison was made for Example 5, which gave in general similar results. The typically higher number of equations results from the various water fronts, and the oil bank. The increase from 5a to 5d is higher than for the KOPT code (2a to 2d), because more oil characteristics are needed to simulate the decaying oil bank. One notable fact is that when no mass balance computations were performed for example 5f, the average CPU time dropped to 180.89 seconds. The increase in efficiency is obtained at the cost of knowing how accurate the solution is.

In the land treatment cases, no oil equations are solved. The computation time for the volatile constituent is much higher than that for the nonvolatile one, due to the high volatile fluxes that occur each time the plow zone is cultivated. More time is needed for the randomly generated rainfalls, because of the greater number of rainfall events and the occasionally higher fluxes than in the controlled column study.

SECTION 7

DISCUSSION AND CONCLUSIONS

This work has shown that kinematic theory can be applied to multiphase flow problems. Kinematic models have an advantage over traditional numeric models in that the kinematic models are well-suited for studying the hyperbolic or wave behavior of the multiphase flow equations. Inclusion of sharp fronts is natural to the kinematic models, while finite difference or finite element models encounter difficulties when derivatives in the governing equations tend to become undefined. Solution of the kinematic model shows how the oil and water fronts interact. Thus by simplifying the governing equations, some of the fundamental behavior of the solution is clearly revealed. The effect of the neglected capillary pressure gradients are to increase the infiltration capacity of the soil (accounted for by Charbeneau et al., 1988) and smear the fronts. Much of the important physics is retained, however, in the kinematic model.

Computationally, by reducing the original system of coupled partial differential equations to a system of ordinary differential equations, the difficulty of finding a numerical solution is reduced greatly. Resulting computer codes are well suited to solving problems where there is a constant amount of water in the pore space. Such a situation corresponds to a soil at the so-called field capacity and can represent typical conditions of the profile. The best performance of the KOPT model is obtained when the oil is nondegrading and the oil characteristics are straight. Curving characteristics, due to biodegradation, increase the computational effort.

The implementation of the more general model (KROPT) reveals the interactions between the oil and water fronts. The model is limited to situations where the initial water profile is uniform. Once again the best performance is obtained when the oil characteristics are straight, since the characteristic equations are not solved explicitly. Performance is degraded where rainfalls exceed the kinematic capacity of the soil. Since the infiltration capacity is infinite initially, very large water fluxes are possible until runoff is produced. During this period small time steps are required.

Two categories of conclusions will be discussed:

- physical phenomena occurring in multiphase flow,
- numerics of the methods selected for the solution.

PHYSICAL PHENOMENA OCCURRING IN MULTIPHASE FLOW

This modeling work enhances understanding of multiphase flow through the results obtained from the example problems presented in Section 6. Most important is the material concerning the oil banks. If incoming rainfalls displace oil, then the banks are created. Although this is a result of simplified modeling, the notion that incoming water displaces oil into a bank, moving ahead of the water front, is a more general result. In situations where the flow of the fluids is not kinematic, banks will also exist. In certain cases, the banks may be very pronounced, although short lived. In others the banks may persist for longer periods, but would be virtually undetectable in the laboratory and the field or by numerical methods that are not based upon the kinematic model.

The kinematic model results indicate that the water displaces all of the mobile oil. This result was contrary to what was expected, but was established through conservation of mass. Some displacement of oil would be expected, along with the creation of an oil bank, but the model result may or may not be confirmed by experiment.

The value of S_{or} is critical for the results obtained from the model. This parameter could be easily manipulated to show that oil would spread over a smaller depth (see equation 52).

Biodegradation of the oil has only a small effect upon the ultimate depth attained by the oil. It does effect the mobility of the oil (reducing it). An interesting effect on the constituent is caused by biodegradation of the oil. Concentrations increase as the oil degrades because of the loss of solvent. If the constituent is also biodegradable, the shorter half life determines if the concentration will increase or not.

As in field cases, where constituent concentrations in water are measured, a large mass of constituent may reside in the oil phase and not be detected. In example 2 concentrations in the oil are 50 times greater than in the water. If only the water phase concentrations are measured, most of mass in the soil is missed. This is particularly a problem if the oil is immobilized, since the oil cannot flow into an observation well (phenomena akin to end effects may prevent oil flow into wells even at higher saturations). The presence of the oily material is not detected by the observation wells; the core material itself must be analyzed.

NUMERICS OF THE METHODS SELECTED FOR THE SOLUTION

Using a differential equation solver is well suited to solving the kinematic model, since the model equations can be written as a system of ordinary differential equations. The speed of the solver is degraded as more and more equations are added. For these situations, it might be advantageous to solve the method of characteristics portion of the solution by finite difference techniques instead of tracking the characteristics. The overhead associated with using the RKF solver may be comparable to that for the discretization methods. Also, the necessity to track sets of oil bank characteristics makes the program exceedingly complex. Extension of the model as discussed below may not be practical, because of this.

Severe difficulties are encountered in solving the oil equations when the initial water profile is not constant. This occurs because the slope of the water profile is infinite at the surface. The term in the method of characteristics solution that gives the change in oil saturation (equation 20) has an infinite negative slope as the solution commences. Modification of the model so as to ignore this allows a solution to be obtained, but that solution does not conserves mass.

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APPENDIX A

KOPT USERS GUIDE

PROGRAM KOPT USERS GUIDE

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The program KOPT (Kinematic Oily Pollutant Transport) was developed for simulation of the fate and multiphase transport of hydrocarbons within the vadose zone. These hydrocarbons may have been released through leaking tanks and spills or applied during land treatment of organic wastes. KOPT applies kinematic modeling theory to simulate the migration of a hydrocarbon phase (referred to as an "oil") and a dissolved constituent as they migrate through the vadose zone under the force of gravity. Water movement is considered to occur at the average annual infiltration rate. The dissolved constituent is free to partition within the oil-water-air-soil system according to linear local equilibrium assumptions. The model includes the processes of volatilization, sorption of the dissolved constituent, and degradation of both the dissolved constituent and the oil. The simulation model provides the concentration and hydrocarbon profiles at any time as well as the hydrocarbon and constituent flux past any horizon as a function of time. KOPT was developed under funding from both the U.S. Environmental Protection Agency and the Texas Water Development Board. It is written in Standard Fortran 77 and will run on PC or mainframe computers.

The Input Data File

The input data for KOPT is contained in a file called "INPUT.KOP" which is free format and is opened and read by the program. This file must be developed by the user and stored on the same directory as the executable code. The program creates a file "OUTPUT.KOP" and saves the program output on it. The output file can be edited or printed. Each card of the input file is described below.

Card 1-3. Run Title

RUN TITLE (3 LINES OF UP TO 50 CHARACTERS EACH)

Card 4. Matrix Properties

WKS, XLAMB, ETA, RHOS, SWR

WKS	saturated hydraulic conductivity (water)
XLAMB	pore size distribution index (Brooks & Corey's l)
ETA	porosity
RHOS	bulk density of matrix
SWR	residual water saturation

Card 5. Water Properties

WMU, WRHO, IRT, QW or SWMAX

WMU	dynamic viscosity of water
WRHO	density of water
IRT	rainfall input type: 1=flux specified 2=saturation specified
QW or SWMAX	constant water flux or saturation

Card 6. Oil Characteristics

PMU, PRHO, SPR, HLO, OLAG, IAT

PMU	dynamic viscosity of oil
PRHO	oil density
SPR	residual (trapped) oil saturation
HLO	oil half-life (=0. if non-degrading)
OLAG	acclimation time for biodegradation to begin
IAT	oil input type 1=flux specified 2=volume/area specified 3=constant head

Card 7. (for IAT=1) Oil Flux

QP, TPB, TPE, DPA, IP, HS

QP	oil flux (volume/area/time)
TPB	oil event beginning time
TPE	oil event ending time
DPA	depth at which pollutants are applied
IP	ponding type 0=excess oil runs off surface 1=variable (see note 4.) 3=constant
HS	constant head for IP=3 cases

Card 7. (for IAT=2) Oil Volume

PVOL, DPA, DPL

PVOL	oil volume/area incorporated into the soil
DPA	depth at which pollutants are applied
DPL	lower depth of initially polluted zone

Card 7. (for IAT=3) Constant Head

QP, TPB, TPE, DPA, IP, HS

Same as for IAT=1 except QP is meaningless

Card 8. Dissolved Constituent

COINI, FCV, HLC, CLAG

COINI	initial concentration in oil (see note 5.)
FCV	factor for consistent volume units (see note 5.)
HLC	constituent half-life (=0. if non-degrading)
CLAG	acclimation time for biodegradation to begin

Card 9. Partition Coefficients

XXKO, XXKV, XKOC

XXKO	oil-water partition coefficient
XXKV	air-water partition coef. (Henry's law)
XKOC	soil-water partition coefficient

Card 10. Volatilization Model

DAIR, DWV, EVAP, TEMP, RH, XCF

DAIR	diffusion coef. for constituent in air
DWV	diffusion coef. for water vapor
EVAP	water evaporation rate (vol./area/time)
TEMP	temperature in degrees C
RH	relative humidity
XCF	conversion factor to gm/cc (see note 2.)

Card 11. Simulation Parameters

TM, DM, DTPR

TM	simulation ending time
DM	maximum solution time step
DTPR	minimum time between printed time steps and mass balance checks

Card 12. Profiles and Histories

NTIMES, NZS

NTIMES	number of profiles desired (up to 10)
NZS	number of histories desired (up to 3)

Card 13. Profiles

PR(NTIMES)	profile times

Card 14. Histories

HI(NZS) history depths

Notes

1. All variable names are in accordance with fortran naming - names beginning with I through M are integers, all others are reals.

2. With the following exceptions, all input parameters must be given in a consistent system of units.

- The temperature must be given in degrees C.
- The conversion factor from density units to gm/cc (f/XCF = gm/cc; volatilization model uses an empirical formula for water vapor density).

3. Zeros should be read in fields pertaining to unused values.

4. Variable surface ponding is supported only for cases with no dissolved constituent present.

5. The concentration of the dissolved constituent can be read in any desired units (eg. mg/L). A conversion to the consistent volume unit must be read in variable FCV in order for the calculated mass balances to be correct. For example, with concentration in mg/L = gm/m3 and C-G-S units, then the flux must be multiplied by the number of m2/cm2 and FCV = 0.0001. The output concentration will be in mg/L = gm/m3 while the mass balance will be in mg/cm2.

6. Detailed information on the program KOPT is contained within the Ph.D. dissertation of Weaver (1988).

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APPENDIX B

KOPT PROGRAM LISTING

```
     PROGRAM KOPT
C     **************************************************************
C     **************************************************************
C     *                                                            *
C     *   KOPT   KINEMATIC OILY POLLUTANT TRANSPORT                *
C     *                                                            *
C     *                                                            *
C     *   PURPOSE....THIS PROGRAM SIMULATES THE GRAVITY DOMINATED  *
C     *   ONE DIMENSIONAL DOWNWARD TRANSPORT OF AN OILY GROUND-    *
C     *   WATER POLLUTANT.  THE OIL  MAY CONTAIN A DISSOLVED       *
C     *   CONSTITUENT.  THE MIGRATION OF THESE OCCURS IN THE       *
C     *   PRESENCE OF A CONSTANT AMOUNT OF PORE WATER.  THE CON-   *
C     *   STITUENT IS SUBJECT TO PARITIONING BETWEEN THE OIL,      *
C     *   WATER, SOIL AIR, AND THE SOIL.  BOTH THE OIL AND THE     *
C     *   CONSTIUENT MAY BIODEGRADE OCCORDING TO FIRST ORDER       *
C     *   KINETICS.
C     *                                                            *
C     *   THE SOLUTION IS OBTAINED VIA A RUNGE-KUTTA-FEHLBERG IN-  *
C     *   TEGRATION OF A SYSTEM OF COUPLED ORDINARY DIFFERENTIAL   *
C     *   EQUATIONS.  A GUIDE TO THE REQUIRED INPUT DATA CAN BE    *
C     *   FOUND IN THE SOURCE CODE FOR THE INPUT SUBROUTINE.       *
C     *   OUTPUT IS PRODUCED IN THREE FILES WHICH CONTAIN          *
C     *   THE LOCATION OF THE DEEPEST EDGE OF THE POLLUTANT AT ALL *
C     *   TIMES, PROFILES AT VARIOUS TIMES AND HISTORIES AT VAR-   *
C     *   IOUS DEPTHS.                                             *
C     *                                                            *
C     **************************************************************
C     *   WARNING:  THE RESULTS FROM THIS CODE HAVE NOT BEEN       *
C     *   VERIFIED BY EITHER LABORATORY OR FIELD STUDIES.  THE     *
C     *   SUITIBILITY OF THIS PROGRAM FOR ANY PURPOSE IS NOT IM-   *
C     *   PLIED.    THE AUTHOR ACCEPTS NO LIABILITY RESULTING FROM *
C     *   ITS USAGE.                                               *
C     **************************************************************
C     *                                                            *
C     *   AUTHOR  JIM WEAVER                                       *
C     *           THE UNIVERSITY OF TEXAS AT AUSTIN                *
C     *                                                            *
C     *                                                            *
C     *   SINGLE PRECISION, ANSI STD. X3.9-1978 FORTRAN 77         *
C     *   REQUIRED ROUTINES...BLOCK DATA ONE,PFRONT,PCHK,GACHK,    *
C     *     GAHS,RD,CVEL,CONC,OCP,ZMASS,OIL,HIST,SFLUX,INPUT,START,*
C     *     COUNT,MRKF12,GLQ,INQUAD(INQSET),BINARY,BISEC,WKE(PKE,  *
C     *     SLOPE,KRSET)                                           *
C     *   OCTOBER 21, 1987                                         *
C     **************************************************************
C     **************************************************************
      DIMENSION NEQ(3),YY(55,3)
      COMMON /COUN/ IPR(60),NUM(60),SEC(60)
      COMMON /OUTP/ ERCMX,EROMX,NPT,NREG
      COMMON /POLL/ DPA,DPL,DTP,DZPMDT,DZPDDT,IAT,PKS,PVOL,QP,SPMAX,SPR,
     1              THPZ,TPB,TPE,TPR,WP(50),XKPMX,XK22
      COMMON /SIMU/ DM,DTPR,TM
      EXTERNAL PCHK,PFRONT
      DATA ND /55/
      NUM(1) = 1
C
      CALL INPUT
      CALL START (NEQ,YY,ND)
```

```
C
C     ***POLLUTANT AND DISSOLVED CONSTITUENT COMPUTATIONS
      CALL MRKF12 (PFRONT,PCHK,TPB,TM,DM,1.E-5,NEQ,NPT,NREG,YY,ND,ET)
C
      CALL COUNT
      END
      BLOCK DATA ONE
      COMMON /COUN/ IPR(60),NUM(60),SEC(60)
      COMMON /TRIAL/ DTOLD, DTOLD1, ICC, TEND, ICHAR
      COMMON /VAPO/ ABL,AKS,CN,CV(2),CVF(2),DAIR,XJV(2),ZV(2)
      COMMON /OUTP/ ERCMX,EROMX,NPT,NREG
      COMMON /FRNT/ ISE,PF(2),PS(2),PT(2),PZ(2)
      COMMON /GAEQ/ CHS(2),DO,EE,FF,GA1,GA2,GA3,GA4,HS,IGA,IP,ZGA
      COMMON /POLL/ DPA,DPL,DTP,DZPMDT,DZPDDT,IAT,PKS,PVOL,QP,SPMAX,SPR,
     1              THPZ,TPB,TPE,TPR,WP(50),XKPMX,XK22
      DATA NUM /60*0/
      DATA DZPMDT, NPT, ISE /0., 2, 0/
      DATA DPA,DPL,HS,THPZ,TPB,TPE,QP,IP /7*0.,0/
      DATA  CVF,XJV /4*0./
      DATA ERCMX,EROMX /2*0./
      DATA DTOLD1,ICC,ICHAR /0.,2*0/
      END
      SUBROUTINE PFRONT (TT,ZZ,F,ND,NEQ)
C     *****************************************************************
C     *                                                               *
C     *   PFRONT   POLLUTANT FRONT                                    *
C     *                                                               *
C     *                                                               *
C     *   PURPOSE....THIS SUBROUTINE CONTAINS THE FUNCTIONS F(Y,T) *
C     *   FOR THE OIL AND CONSTITUENT EQUATIONS THAT ARE USED BY  *
C     *   MRKF12.                                                     *
C     *   THE EQUATIONS ARE DIVIDED INTO 3 GROUPS AS FOLLOWS          *
C     *   GROUP 1.  #1 OIL FRONT  #2 VOLATILE FRONT                   *
C     *   GROUP 2.  OIL CHARACTERISTICS                               *
C     *             FROM THE SURFACE (#1) TO THE OIL FRONT (UP    *
C     *             TO #51)                                           *
C     *   GROUP 3.  CONSTITUENT CHARACTERISTICS                       *
C     *             FROM THE FRONT (#1) TO THE TOP (#11 OR #15)   *
C     *   THIS ARRANGEMENT ALLOWS THE MRKF12 ROUTINE TO VARY THE  *
C     *   NUMBER OF EQUATIONS SOLVED EASILY                           *
C     *                                                               *
C     *   INPUT ARGUMENTS........................................    *
C     *   TT      = TIME                                              *
C     *   ZZ(I,J) = DEPTH FOR EQUATION I OF GROUP J                   *
C     *   ND      = ROW DIMENSION OF ZZ                               *
C     *   NEQ(3)  = ARRAY OF NUMBER OF EQUATIONS FOR EACH GROUP   *
C     *                                                               *
C     *   OUTPUT ARGUMENTS.......................................    *
C     *   F(I,J) = FUNCTION VALUE FOR EQUATION I OF GROUP J           *
C     *   NEQ(3) = NUMBER OF EQUATIONS PER GROUP                      *
C     *                                                               *
C     *                                                               *
C     *   AUTHOR  JIM WEAVER                                          *
C     *           THE UNIVERSITY OF TEXAS AT AUSTIN                   *
C     *                                                               *
C     *   SINGLE PRECISION, ANSI STD. X3.9-1978 FORTRAN 77        *
C     *   REQUIRED ROUTINES...SLOPE,BISEC,GAHS,INQUAD,PKE,OIL,CVEL *
C     *     RD,CONC                                                   *
```

```
C     *   X-21-87                                                        *
C     *                                                                  *
C     ********************************************************************
      DIMENSION F(ND,*),NEQ(*),ZZ(ND,*)
      COMMON /CCHR/ CPART,CC(75,2),C0(75),TC(75),ZC(75,2)
      COMMON /COUN/ IPR(60),NUM(60),SEC(60)
      COMMON /CONCI/ CLAG,COINI,DLC,FCV,XSF1,XXKV,XXKW
      COMMON /FRNT/ ISE,PF(2),PS(2),PT(2),PZ(2)
      COMMON /GAEQ/ CHS(2),DO,EE,FF,GA1,GA2,GA3,GA4,HS,IGA,IP,ZGA
      COMMON /MATR/ ETA,OMSOR,OMSWR,SR,SWR
      COMMON /OCHR/ DLO,OLAG,SI(75,2),S0(75),T0(75),ZI(75,2)
      COMMON /POLL/ DPA,DPL,DTP,DZPMDT,DZPDDT,IAT,PKS,PVOL,QP,SPMAX,SPR,
     1              THPZ,TPB,TPE,TPR,WP(50),XKPMX,XK22
      COMMON /VAPO/ ABL,AKS,CN,CV(2),CVF(2),DAIR,XJV(2),ZV(2)
      COMMON /WTER/ IRT,SWMAX,QW,WKS
      EXTERNAL GAHS
C
      NUM(2) = NUM(2) + 1
      PT(2) = TT
      ISE = ISE + NEQ(1)+NEQ(2)+NEQ(3)
C
C     ***CHARACTERISTICS FOR DEGRADING OILS
      DO 10 I=1,NEQ(2)
        F(I,2) = 0.
        SI(I,2) = SPR
        ZI(I,2) = DPA
        IF (TT.LT.T0(I)) GO TO 10
        XXX = 1.
        IF (TT.GT.OLAG) THEN
          TAU = AMAX1(OLAG,T0(I))
          XXX = EXP(-DLO*(TT-TAU))
        END IF
        SP  = S0(I)*XXX
        SI(I,2) = SP
        ZI(I,2) = ZZ(I,2)
        CALL SLOPE (0,SP,0,SWMAX,SL,0.,0)
        F(I,2) = SL/ETA
 10   CONTINUE
      ZS = DPA + (TT-TPE)*DZPDDT
C
C     ***THE OIL FRONT
      F(1,1) = 0.
      IQF = 1
      IF (DLO.EQ.0.) THEN
C       ***NON-DEGRADING OILS
        IF (IGA.EQ.1) THEN
          DTX = TT - TPB
          IF (DTX.GT.DTP) DTX = DTP
          IHS = 0
          IF (IP.EQ.3) THEN
            CHS(2) = HS
            IF (TT.GT.TPE) CHS(2) = 0.
          ELSE
            CHS(2) = QP*DTX - (ZZ(1,1)-DPA)*SPMAX*ETA
            IF (CHS(2).LT.0.) CHS(2) = 0.
            IF (CHS(1).GT.0..AND.CHS(2).LE.0.) IHS = 1
          END IF
        END IF
        IF (ZS.LT.ZZ(1,1).OR.CHS(2).GT.0..OR.IHS.EQ.1) THEN
C         ***CONSTANT MAXIMUM OIL SATURATION
          SPF = SPMAX
          IF (IGA.EQ.1.AND.CHS(2).GT.0.) THEN
C           ***PRESSURIZED CONDITIONS
            IF (IP.EQ.1) THEN
              T1 = TT - TPB
              IF (T1.GT.DTP) T1 = DTP
              QPF = EE + FF*T1/(ZZ(1,1)-DPA)
            ELSE IF (IP.EQ.3) THEN
C             ***ANALYTIC SOLUTION FOR FRONT WITH CONSTANT DEPTH PONDING
              ISE = ISE - 1
              Z2 = ZGA*5.
              IF (PZ(1).GE.ZGA) Z2 = PZ(1)*10.
              CALL BISEC (GAHS,PZ(1),Z2,0.0001,75,0,TT-TPB,GA1,
     1        ZZ(1,1),DT,IE)
              IF (ZZ(1,1).GT.DPA) QPF = XKPMX*(1.+CHS(2)/(ZZ(1,1)-DPA))
              IQF = 0
            END IF
          ELSE
C           ***GRAVITY DOMINATED FLOW
            QPF = XKPMX
          END IF
        ELSE
C         ***GRAVITY DRAINAGE
          SL = (ZZ(1,1)-DPA)/(TT-TPE)
          CALL INQUAD (WP,50,SPR,1.-SWMAX,SL*ETA,SPF)
          CALL PKE (0,SPF,0,SWMAX,QPF,0.,0)
        END IF
      ELSE IF (DLO.NE.0.) THEN
C       ***DEGRADING OILS
        CHS(2) = 0.
        SL = 0.
        S1 = SPMAX
        LZ = NEQ(2)
        DO 20 I=NEQ(2),2,-1
          IF (ZI(I,2).GE.ZZ(1,1).AND.ZZ(1,1).GT.ZI(I-1,2)) THEN
            LZ = I
            GO TO 21
          END IF
 20     CONTINUE
 21     CONTINUE
        IF (TT.GT.TO(LZ-1)) S1 = SI(LZ-1,2)
        IF (ZI(LZ,2).NE.ZI(LZ-1,2))
     1  SL = (S1-SI(LZ,2))/(ZI(LZ-1,2)-ZI(LZ,2))
        SPF = SI(LZ,2) + (ZZ(1,1)-ZI(LZ,2))*SL
        QPF = 0.
        IF (SPF.GT.SPR) CALL PKE (0,SPF,0,SWMAX,QPF,0.,0)
      END IF
      IF (IAT.EQ.2.AND.QP.EQ.0.) THEN
        XXX = 1.
        IF (TT.GT.OLAG) XXX = EXP(-DLO*(TT-OLAG))
        SPF = SPMAX*XXX
      END IF
      IF (IQF.EQ.1.AND.QPF.GT.0.) F(1,1) = QPF/SPF/ETA
      PS(2) = SPF
      PZ(2) = ZZ(1,1)
      PF(2) = QPF
```

```
C
C     ***DISSOLVED CONSTITUENTS
C     ***CHARACTERISTICS
      DO 50 I=1,NEQ(3)
        F(I,3) = 0.
        ZC(I,2) = DPA
        IF (TT.LT.TC(I)) GO TO 50
        CALL OIL (ZZ(I,3),TT,SWMAX,NEQ(2),SO)
        IF (ABS(TT-TPE).LE.0.0001.AND.I.EQ.NEQ(3)) SO = SPR
        CALL CVEL (TT,SO,SWMAX,F(I,3))
        XXX = 1.
        YYY = 1.
        IF (DLC.GT.0..AND.TT.GE.CLAG) XXX = EXP(-DLC*(PT(2)-PT(1)))
        IF (DLO.GT.0..AND.SO.GT.0..AND.TT.GT.OLAG) THEN
C         ***CORRECTION FOR OIL DECAY
          SO2 = SO/EXP(  -DLO*(PT(2)-PT(1))  )
          YYY = RD(SO2,SWMAX)/RD(SO,SWMAX)
        END IF
        CC(I,2) = CC(I,1)*XXX*YYY
        ZC(I,2) = ZZ(I,3)
 50   CONTINUE
      F(2,1) = 0.
      IF (TT.LT.TPE.OR.XXKV.LE.0..OR.CC(1,2).LT.5.E-5.OR.NEQ(1).LT.2)
     1RETURN
C
C     ***VOLATILIZATION
      CALL OIL (ZZ(2,1),TT,SWMAX,NEQ(2),SO)
      IF (ABS(TT-TPE).LT.0.0001.AND.ZZ(2,1).LE.DPA+0.0001) SO = SPR
      CALL CONC (TT,ZZ(2,1),SWMAX,SO,NEQ(3),CX,XX,0)
      CALL CVEL (TT,SO,SWMAX,F(2,1))
      IF (ABS(TT-TPE).LE.1.E-4.AND.CX.LE.0.) CX = CPART
C     ***DIFFUSIVE FLUX
      DSOIL = DAIR*((ETA*(1.-SWMAX-SO))**CN)/ETA/ETA
      CXV = XXKV*CX
      D1 = DSOIL*ABL + DAIR*ZZ(2,1)
      IF (D1.GT.0.) XJV(2) = CXV*DSOIL*DAIR/D1
C     ***CUMULATIVE VOLATILE FLUX
      CVF(2) = CVF(1) + (TT-PT(1))*0.5*(XJV(2)+XJV(1))*FCV
      IF (CX.GT.0.)
     1F(2,1) = F(2,1) + XJV(2)/RD(SO,SWMAX)/CX
      CV(2) = CX
      ZV(2) = ZZ(2,1)
      RETURN
      END
      SUBROUTINE PCHK (TT,ZZ,Z1,ND,NEQ,DMAX,DT,DTR,NS,IC,IRR,IR,IRP)
C     **************************************************************
C     *                                                            *
C     *   PCHK                                                     *
C     *                                                            *
C     *                                                            *
C     *   PURPOSE....THIS SUBROUTINE CONTAINS A SERIES OF CHECKS   *
C     *   AND CONTROLS FOR THE SOLUTION OF THE KINEMATIC MODEL.    *
C     *   IF A STEP IS NOT REJECTED BY PCHK OR MRKF12, THEN RESULTS*
C     *   FOR THE CURRENT STEP ARE OUTPUT AND VARIOUS VALUES ARE   *
C     *   ROLLED FOR THE NEXT EVALUATION.                          *
C     *                                                            *
C     *   INPUT ARGUMENTS.......................................   *
C     *   TT      = SOLUTION TIME JUST OBTAINED                    *
```

```
C     *   ZZ(I,J) = DEPTH FOR EQUATION I GROUP J                         *
C     *   Z1(I,J) = PREVIOUS DEPTH FOR EQUATION I GROUP J                *
C     *   ND      = ROW DIMENSION OF ZZ()                                *
C     *   NEQ(3)  = NUMBER OF EQUATION IN EQCH GROUP                     *
C     *   DMAX    = MAXIMUM TIME STEP                                    *
C     *   DT      = CURRENT TIME STEP                                    *
C     *   NS      = NUMBER OF STEPS                                      *
C     *   IRP     = 1 IF MRKF12 ALREADY HAS REJECTED THE STEP            *
C     *                                                                  *
C     *   OUTPUT ARGUMENTS.........................................      *
C     *   NEQ(3)  = ADJUSTED NUMBER OF EQUATIONS                         *
C     *   DMAX    = ADJUSTED MAX. TIME STEP                              *
C     *   DT      = NEW TIME STEP FOR ACCEPTED STEPS                     *
C     *   DTR()   = SERIES OF PROPOSED REDUCED TIME STEPS                *
C     *   IC      = 1 TO END SIMULATION                                  *
C     *   IRR()   = CODES CORESPONDING TO VARIOUS REDUCED STEPS          *
C     *   IR      = 1 TO REJECT STEP                                     *
C     *                                                                  *
C     *                                                                  *
C     *   AUTHOR  JIM WEAVER                                             *
C     *           THE UNIVERSITY OF TEXAS AT AUSTIN                      *
C     *                                                                  *
C     *   SINGLE PRECISION, ANSI STD. X3.9-1978 FORTRAN 77               *
C     *   REQUIRED ROUTINES...SFLUX,GACHK,ZMASS,COUNT,HIST               *
C     *   X-21-87                                                        *
C     *                                                                  *
C     ********************************************************************
      DIMENSION DTR(*),IRR(*),NEQ(*),ZZ(ND,*),Z1(ND,*)
      COMMON /CCHR/ CPART,CC(75,2),C0(75),TC(75),ZC(75,2)
      COMMON /CONCI/ CLAG,COINI,DLC,FCV,XSF1,XXKV,XXKW
      COMMON /COUN/ IPR(60),NUM(60),SEC(60)
      COMMON /FRNT/ ISE,PF(2),PS(2),PT(2),PZ(2)
      COMMON /GAEQ/ CHS(2),DO,EE,FF,GA1,GA2,GA3,GA4,HS,IGA,IP,ZGA
      COMMON /HIPR/ IHIST,NTIMES,PR(10),NZS,HI(5)
      COMMON /MATR/ ETA,OMSOR,OMSWR,SR,SWR
      COMMON /OCHR/ DLO,OLAG,SI(75,2),S0(75),T0(75),ZI(75,2)
      COMMON /OUTP/ ERCMX,EROMX,NPT,NREG
      COMMON /POLL/ DPA,DPL,DTP,DZPMDT,DZPDDT,IAT,PKS,PVOL,QP,SPMAX,SPR,
     1              THPZ,TPB,TPE,TPR,WP(50),XKPMX,XK22
      COMMON /SIMU/ DM,DTPR,TM
      COMMON /VAPO/ ABL,AKS,CN,CV(2),CVF(2),DAIR,XJV(2),ZV(2)
      COMMON /WTER/ IRT,SWMAX,QW,WKS
      COMMON /TRIAL/ DTOLD, DTOLD1, ICC, TEND, ICHAR
      DATA I1,I2,I4,T2 /2,1,1,0./
C
C     ***SR PCHK PART 1.)  VARIOUS RKF CONTROL CHECKS
      NUM(3) = NUM(3) + 1
      IF (NUM(3).EQ.1) DTOLD = DMAX
C
C     ***ASSURE AT LEAST 5 STEPS THROUGH OIL APPLICATION
      IF (IRR(6).EQ.0.AND.DMAX.GT.0.75*DTP.AND.IAT.NE.2) THEN
        DTOLD = DMAX
        DMAX = DTP*.2
        DTR(6) = DT
        IRR(6) = 1
        IR = 1
      END IF
C
```

```
C     ***CHECK FOR POLLUTANT ENDING TIME
      IF (IRR(4).EQ.0..AND.IAT.NE.2) THEN
        IF (TT.EQ.TPE) THEN
          IRR(4) = 1
        ELSE IF (TT.GT.TPE) THEN
          IR = 1
          DTR(4) = TPE - PT(1)
        END IF
      END IF
C
      T1 = TPE
      IF (IGA.EQ.1.AND.IP.EQ.1.AND.CHS(2).GT.0.) T1 = 2.*TT
      IF (((COINI.GT.0..AND.I1.LE.NEQ(3)).OR.(DLO.GT.0..AND.I1.
     1LE.10)).AND.PT(1).LE.T1) THEN
C       ***STEP TO THE TIME EACH NEW CHARACTERISTIC STARTS
        IF (TC(2).NE.T0(50).AND.IGA.NE.1) STOP 50
        IF (IRR(5).EQ.0.) THEN
           IF (TC(I1).LT.TT) THEN
C              ***I1 WILL BE INCREMENTED ONLY IF THIS NEW STEP SIZE
DOMINATES
             IF (TC(I1).EQ.PT(1)) GO TO 300
             IR = 1
             DTR(5) = TC(I1)-PT(1)
           END IF
 300       CONTINUE
        END IF
      END IF
C
C     ***IMPROVE ACCURACY IF CONSTITUENT CHARACTERISTICS LEAVE OIL
 305  CONTINUE
      IF (COINI.GT.0..AND.IRR(10).EQ.0.AND.QW.GT.0.) THEN
        IF (ZC(I2,2).GE.PZ(2)) THEN
          IF (ZC(I2,2).EQ.PZ(2)) THEN
            IRR(10) = 1
            GO TO 305
          END IF
          IR = 1
          SL1 = (ZC(I2,2)-ZC(I2,1))/DT
          SL2 = (PZ(2)-PZ(1))/DT
          TNEW = (PZ(1)-ZC(I2,1)+PT(1)*(SL1-SL2))/(SL1-SL2)
          DTR(10) = TNEW-PT(1)
        END IF
      END IF
C
C     ***MAKE LARGE STEP OUTPUT LOOK NICE
      IF (IRR(11).EQ.0.AND.PT(2)-PT(1).GE.DTOLD.AND.TT.GT.TPE) THEN
        DTR(11) = FLOAT(IFIX(PT(2)*10000.)/10000) - PT(1)
        IF (DTR(11).GT.0.) IR = 1
      END IF
C
      IF (DLO.GT.0.) GO TO 310
C
C     ***GREEN-AMPT CHECKS IN SR GACHK
      IF (IGA.EQ.1) CALL GACHK(TT,ZZ,Z1,ND,NEQ,I1,I2,DMAX,DT,DTR,NS,IC,
     1IRR,IR)
C
C     ***END OF MAXIMUM OIL SATURATION
      IF (IRR(2).EQ.0.AND.((TT.GT.TPE.AND.IGA.EQ.0).OR.
     1(CHS(1).LE.0.AND.IGA.EQ.1))) THEN
        IF (PS(1).LT.SPMAX) IRR(2) = 2
        ZS = DPA + (TT-TPE)*DZPDDT
        IF (ZZ(1,1).LT.ZS) THEN
          SL = DZPMDT
          T11 = TPB
          Z11 = DPA
          IF (IGA.EQ.1) THEN
            SL = (PZ(2)-PZ(1))/(PT(2)-PT(1))
            T11 = PT(1)
            Z11 = PZ(1)
          ELSE IF (IAT.EQ.2) THEN
            T11 = TPE
            Z11 = DPL
          END IF
          TNEW = (Z11 - DPA - T11*SL + TPE*DZPDDT)/(DZPDDT - SL)
          DTX = TNEW - PT(1)
          IF (DTX.GT.0.) THEN
            DTR(2) = DTX
            IR = 1
          END IF
        END IF
      END IF
 310  CONTINUE
C
C     ***VOLATILIZATION OF ENTIRE MASS OF CONSTITUENT
      IF (XXKV.GT.0..AND.IRR(3).EQ.0) THEN
        IF (ZV(2).GT.ZC(1,2)) THEN
          IR = 1
          DD = PT(2) - PT(1)
          SL1 = (ZV(2)-ZV(1))/DD
          SL2 = (ZC(1,2)-ZC(1,1))/DD
          TNEW = (ZV(1)-ZC(1,1)+PT(1)*(SL2-SL1))/(SL2-SL1)
          DTR(3) = TNEW - PT(1)
        END IF
      END IF
C
C     ***SIMULATION ENDING TIME
      IF (IRR(12).EQ.0.AND.PT(2).GT.TM) THEN
        IR = 1
        DTR(12) = TM - PT(1)
        IF (DTR(12).EQ.0.) IC = 1
      END IF
C
C     ***PROFILE TIMES
      IF (IRR(13).EQ.0.AND.NTIMES.GT.0) THEN
        IF (TT.GE.PR(I4)) THEN
          DTR(13) = PR(I4) - PT(1)
          IF (ABS(TT-PR(I4)).LT.5.E-5) THEN
            DTR(13) = 1.E19
            IRR(13) = 1
          ELSE
            IR = 1
          END IF
        END IF
      END IF
C
C
```

```
C
C     ***RETURN ANY REJECTED STEP
      IF (IR.EQ.1.OR.IRP.EQ.1) RETURN
C
C
C
C     ***SR PCHK PART 1B.) CORRECTIONS FOR CONDITIONS DETECTED ABOVE
C     ***ASSURE AT LEAST 5 STEPS THROUGH OIL APPLICATION
      IF (IRR(6).EQ.1) THEN
        IF (TT.GE.TPE) THEN
          DMAX = DTOLD
          IRR(6) = 2
        END IF
      END IF
C
C     ***CHECK FOR POLLUTANT ENDING TIME
      IF (IRR(4).EQ.1) THEN
        IRR(4) = 2
        IRR(5) = 1
        DT = 0.0001
        DTOLD = DMAX
C       IF (DLO.LE.0..AND.IP.NE.1.AND.IGA.NE.1) DMAX = 0.05
        IF (XXKV.GT.0..AND.COINI.GT.0.) NEQ(1) = 2
        IF (NEQ(1).EQ.0) THEN
          NEQ(1) = 1
        END IF
      END IF
C
C     ***STEP TO THE TIME EACH NEW CHARACTERISTIC STARTS
      IF (IRR(5).EQ.1) THEN
C       ***CORRECT CONCENTRATIONS FOR GREEN AMPT CASES
        IF (IGA.EQ.1.AND.QW.GT.0..AND.XXKW.GT.0.) THEN
          CALL SFLUX (TC(I1),QO)
          C0(I1) = QO*COINI/(QO + XXKW*QW)
          CC(I1,2) = C0(I1)
        END IF
        I1 = I1 + 1
        IRR(5) = 0
      END IF
C
C     ***IMPROVE ACCURACY IF CONSTITUENT CHARACTERISTICS LEAVE OIL
      IF (IRR(10).EQ.1) THEN
        IRR(10) = 0
        IF (ABS(ZC(I2,2)-PZ(2)).LT.0.005.OR.DTR(10).LT.0.) I2=I2+1
      END IF
C
C     ***MAKE LARGE STEP OUTPUT LOOK NICE
      IF (IRR(11).EQ.1) THEN
        IRR(11) = 2
      ELSE IF (IRR(11).EQ.2) THEN
        IF (PT(2)-PT(1).LT.DTOLD) THEN
          IRR(11) = 0
        END IF
      END IF
C
C     ***GREEN-AMPT CHECKS IN SR GACHK
      IF (IGA.EQ.1) CALL GACHK(TT,ZZ,Z1,ND,NEQ,I1,I2,DMAX,DT,DTR,NS,IC,
     1IRR,IR)
```

```
C
C     ***END OF MAXIMUM OIL SATURATION
      IF (IRR(2).EQ.1) THEN
        IRR(2) = 0
        IF (PS(1).LT.SPMAX) IRR(2) = 2
        DT = 0.0001
C       DMAX = DTOLD
      END IF
C
C     ***VOLATILIZATION OF ENTIRE MASS OF CONSTITUENT
      IF (IRR(3).EQ.1) THEN
        IF (ZV(2).GE.ZC(1,2)) THEN
          IRR(3) = 2
          NEQ(3) = 0
          NEQ(1) = 1
        ELSE
          IRR(3) = 0
        END IF
      END IF
C
C     ***SIMULATION ENDING TIME
      IF (IRR(12).EQ.1) IC = 1
C
C     ***PROFILE TIMES
      IF (IRR(13).EQ.1) THEN
        I4 = I4 + 1
        IRR(13) = 0
        IF (I4.GT.NTIMES) IRR(13) = 2
      END IF
C
C     ***BIODEGRADATION DURING GREEN AMPT CASES
      IF (IRR(8).EQ.1) THEN
        IRR(2) = 0
        IRR(8) = 3
        IF (IP.EQ.1) TPE = TT
        DT = 0.0001
        IF (ICHAR.EQ.1) THEN
          IF (TPE.GT.TC(NEQ(3))) THEN
            NEQ(3) = NEQ(3) + 1
          ELSE
            N1 = NEQ(3)
            DO 20  I=N1,1,-1
              IF (TPE.GT.TC(I)) THEN
                NEQ(3) = I + 1
                GO TO 21
              END IF
 20         CONTINUE
            STOP 'ICHAR-FAIL'
 21         CONTINUE
          END IF
          TC(NEQ(3)) = TPE
          C0(NEQ(3)) = CPART
          CC(NEQ(3),2) = CPART
          ZC(NEQ(3),2) = DPA
        END IF
        IF (DO.GT.0.) THEN
C         ***TURN ON BIODEGRADATION AFTER PRESSURE FLOW STOPS
          DLO = DO
          NEQ(2) = 51
C         ***DEFAULTS FOR CHARACTERISTICS
          DZ = (PZ(2)-DPA)*0.1
          Z  = PZ(2)
          DO 50 I=51,41,-1
            T0(I) = TPE
            ZI(I,1) = Z
            ZI(I,2) = Z
            ZZ(I,2) = Z
            Z = Z - DZ
 50       CONTINUE
          IF (IP.NE.3) THEN
            DO 55 I=1,40
              T0(I) = TPE
              ZI(I,2) = DPA
              ZI(I,1) = DPA
 55         CONTINUE
          END IF
        END IF
      END IF
C
C     ***SR PCHK PART 2.)  DATA OUTPUT FOR ACCEPTED STEPS
      VOL = 0.
      CVL = 0.
      IF (T2+DTPR.LT.PT(2)) THEN
        T2 = PT(2)
        IZZZ = 0
        IF (ABS(TT-2.2461).LE.0.0001) IZZZ = 1
        CALL ZMASS (TT,ZZ(1,1),PS(2),NEQ,IZZZ,VOL,CVL)
        IF (CVL.LT.1.E-10.AND.VOL.LE.1.E-10) CALL COUNT
        ZZ1 = PZ(2)
        ZZ2 = ZC(1,2)
        ZZ3 = ZC(NEQ(3),2)
        CCC = CC(1,2)*XXKW
        IF (VOL.LE.1.E-10) ZZ1 = 0.
        IF (XXKV.GT.0.AND.ZV(2).GT.ZZ3) ZZ3 = ZV(2)
        IF (CVL.LT.1.E-10) THEN
          ZZ2 = 0.
          ZZ3 = 0.
          CCC = 0.
        END IF
        WRITE (6,9300) NS,TT,ZZ1,CHS(2),PS(2),PF(2),VOL,ZZ2,ZZ3,CCC,CVL,
     1  CVF(2)
      END IF
C     ***HISTORIES
      IF (IHIST.NE.0) CALL HIST (ZZ,Z1,ND,NEQ,TT)
C     ***PROFILES
      DO 25 I=1,NTIMES
        T1 = PT(1)
        IF (T1.LT.PR(I).AND.PR(I).LE.TT) THEN
          DA = PT(2) - PT(1)
          ZP = Z1(1,1)+(PR(I)-T1)*(ZZ(1,1)-Z1(1,1))/DA
          SP = PS(1)+(PR(I)-T1)*(PS(2)-PS(1))/DA
          CALL ZMASS (PR(I),ZP,SP,NEQ,1,VOL,CVL)
        END IF
  25  CONTINUE
C
C
```

```
C     ***SR PCHK PART 3.) ROLL VALUES FOR NEXT EVALUATION
      PT(1) = PT(2)
      PS(1) = PS(2)
      PZ(1) = PZ(2)
      PF(1) = PF(2)
      DO 2 I=1,NEQ(2)
        SI(I,1) = SI(I,2)
        ZI(I,1) = ZI(I,2)
 2    CONTINUE
      DO 4 I=1,NEQ(3)
        CC(I,1) = CC(I,2)
        ZC(I,1) = ZC(I,2)
 4    CONTINUE
      CHS(1) = CHS(2)
      IF (XXKV.GT.0..AND.TT.GT.TPE) THEN
        ZV(1) = ZV(2)
        CV(1) = CV(2)
        XJV(1) = XJV(2)
        CVF(1) = CVF(2)
      END IF
      IF (DLO.EQ.0.) RETURN
      IF (ZZ(NEQ(2)-1,2).GT.ZZ(1,1)) NEQ(2) = NEQ(2) - 1
 9300 FORMAT (1X,I5,11F10.4)
      RETURN
      END
      SUBROUTINE GACHK (TT,ZZ,Z1,ND,NEQ,I1,I2,DTMAX,DT,DTR,NS,IC,IRR,IR)
      DIMENSION DTR(*),IRR(*),NEQ(*),ZZ(ND,*),Z1(ND,*)
      COMMON /CCHR/ CPART,CC(75,2),C0(75),TC(75),ZC(75,2)
      COMMON /CONCI/ CLAG,COINI,DLC,FCV,XSF1,XXKV,XXKW
      COMMON /COUN/ IPR(60),NUM(60),SEC(60)
      COMMON /FRNT/ ISE,PF(2),PS(2),PT(2),PZ(2)
      COMMON /GAEQ/ CHS(2),DO,EE,FF,GA1,GA2,GA3,GA4,HS,IGA,IP,ZGA
      COMMON /MATR/ ETA,OMSOR,OMSWR,SR,SWR
      COMMON /OCHR/ DLO,OLAG,SI(75,2),S0(75),T0(75),ZI(75,2)
      COMMON /TRIAL/ DTOLD, DTOLD1, ICC, TEND, ICHAR
      COMMON /POLL/ DPA,DPL,DTP,DZPMDT,DZPDDT,IAT,PKS,PVOL,QP,SPMAX,SPR,
     1               THPZ,TPB,TPE,TPR,WP(50),XKPMX,XK22
C     ***GREEN-AMPT CHECKS
      NUM(4) = NUM(4) + 1
      IF (TT.LT.TEND) IRR(8) = 0
      IF (IRR(8).EQ.3.OR.PT(2).LT.TPE) RETURN
      IF (IP.EQ.3.AND.PT(1).GE.TPE) IRR(8) = 1
C     ***EXTRA CHARACTERISTICS FOR THE CONSTITUENT IN GREEN-AMPT FLOW
      IF (IP.EQ.1.AND.CHS(2).GT.0..AND.COINI.GT.0.) THEN
        ICHAR = 1
        N1 = NEQ(3)
        DO 10 I=N1,50
          IF (TC(NEQ(3)).LT.TT) THEN
            NEQ(3) = NEQ(3) + 1
            TC(NEQ(3)) = TC(NEQ(3)-1)+DTP*0.1
            C0(NEQ(3)) = CPART
            CC(NEQ(3),2) = CPART
            ZC(NEQ(3),2) = DPA
            Z1(NEQ(3),3) = DPA
            IR = 1
            DTR(9) = DT
          ELSE
            GO TO 15
          END IF
 10     CONTINUE
C       ***ELIMINATE EVEN NUMBERED CHARACTERISTICS
        IE = 2
        DO 12 I=3,51,2
          TC(IE) = TC(I)
          C0(IE) = C0(I)
          ZC(IE,2) = ZC(I,2)
          ZC(IE,1) = ZC(I,1)
          CC(IE,2) = CC(I,2)
          CC(IE,1) = CC(I,1)
          ZZ(IE,3) = ZZ(I,3)
          Z1(IE,3) = Z1(I,3)
          IE = IE + 1
 12     CONTINUE
        NEQ(3) = IE - 1
C       ***CORRECT INTEGERS FOR PCHK CHECKS
        I1 = NEQ(3) - 1
        IF (MOD(I2,2).EQ.0.) I2 = I2 + 1
        IS = 1
        NN = 1
 2      CONTINUE
          IF (IS.EQ.I2) GO TO 3
          NN = NN + 1
          IS = IS + 2
          GO TO 2
 3      CONTINUE
        I2  = I2 - NN + 1
 15     CONTINUE
      END IF
      IF (IP.EQ.1.AND.IRR(7).EQ.0.AND.TT.GE.TPE) THEN
C       ***APPROXIMATE TIME OF ZERO SURFACE PONDING
        IF (CHS(2).LE.0.AND.ICC.EQ.0) THEN
          IR = 1
          DTOLD1 = DTMAX
          DTR(7) = 0.0001
        END IF
      ELSE IF (IRR(7).EQ.1) THEN
        IRR(2) = 5
        IRR(7) = 2
        ICC = 1
        DTMAX = 0.05
      END IF
      IF (IRR(8).EQ.0.AND.ICC.EQ.1.AND.CHS(2).LE.0.) THEN
C       ***TIME OF ZERO SURFACE PONDING
        IF (ZZ(1,1).GE.ZGA) THEN
          SL =  (PZ(2) - PZ(1))/(PT(2) - PT(1))
          IR = 1
          DTR(8) = (ZGA - PZ(1))/SL
          TEND = PT(1) + DTR(8)
          RETURN
        END IF
      ELSE IF (IRR(8).EQ.1) THEN
        IF (DTOLD1.GT.0.) DTMAX = DTOLD1
      END IF
      RETURN
      END
      SUBROUTINE GAHS (IS,ZZ,NN,XY,DT,XX,IE)
      COMMON /COUN/ IPR(60),NUM(60),SEC(60)
      COMMON /GAEQ/ CHS(2),DO,EE,FF,GA1,GA2,GA3,GA4,HS,IGA,IP,ZGA
      COMMON /POLL/ DPA,DPL,DTP,DZPMDT,DZPDDT,IAT,PKS,PVOL,QP,SPMAX,SPR,
     1              THPZ,TPB,TPE,TPR,WP(50),XKPMX,XK22
      NUM(5) = NUM(5) + 1
C     ***ANALYTIC SOLUTION OF THE GREEN AMPT MODEL WITH CONSTANT PONDING
DEPTH
      GA5 = ALOG(ZZ+GA3)
      DT = GA1*(ZZ - GA3*GA5 - GA4 - DPA*(GA5-GA2))
      RETURN
      END
      FUNCTION RD(SO,SW)
      COMMON /COUN/ IPR(60),NUM(60),SEC(60)
      COMMON /CONCI/ CLAG,COINI,DLC,FCV,XSF1,XXKV,XXKW
      COMMON /MATR/ ETA,OMSOR,OMSWR,SR,SWR
C     ***RETARDATION FACTOR
      NUM(6) = NUM(6) + 1
      RD = ETA*(SW*XXKW+SO+XSF1)
      RETURN
      END
      SUBROUTINE CVEL (TT,SO,SW,DZCDT)
      COMMON /COUN/ IPR(60),NUM(60),SEC(60)
      COMMON /CONCI/ CLAG,COINI,DLC,FCV,XSF1,XXKV,XXKW
      COMMON /FRNT/ ISE,PF(2),PS(2),PT(2),PZ(2)
      COMMON /GAEQ/ CHS(2),DO,EE,FF,GA1,GA2,GA3,GA4,HS,IGA,IP,ZGA
      COMMON /MATR/ ETA,OMSOR,OMSWR,SR,SWR
      COMMON /POLL/ DPA,DPL,DTP,DZPMDT,DZPDDT,IAT,PKS,PVOL,QP,SPMAX,SPR,
     1              THPZ,TPB,TPE,TPR,WP(50),XKPMX,XK22
      COMMON /WTER/ IRT,SWMAX,QW,WKS
C     ***CONCENTRATION VELOCITY
      NUM(7) = NUM(7) + 1
      QWC = QW
      IF (IGA.EQ.1.AND.CHS(2).GT.0.) THEN
C       ***PRESSURE FLOW
        QOC = 0.
        IF (SO.GT.SPR) THEN
          QOC = PF(2)
          IF (TT.LT.PT(2)) THEN
            IF (TT.LT.PT(1)) STOP 'CVEL-TIME'
            SL = (PF(2)-PF(1))/(PT(2)-PT(1))
            QOC = PF(1) + (TT-PT(1))*SL
          END IF
        END IF
      ELSE
C       ***KINEMATIC FLOW
        CALL PKE (0,SO,0,SW,QOC,0.,0)
      END IF
      DZCDT = (QWC*XXKW + QOC)/RD(SO,SW)
      RETURN
      END
      SUBROUTINE CONC (TT,ZZ,SW,SO,NEQ3,CO,CMSS,IV)
C     **************************************************************
C     *                                                            *
C     *   CONC                                                     *
C     *                                                            *
C     *   CONC DETERMINES THE OIL PHASE CONCENTRATION AT TIME TT   *
C     *   AND DEPTH ZZ.  OTHER NEEDED INFORMATION ARE THE WATER    *
C     *   AND OIL SATURATIONS (SW,SO) AND THE NUMBER OF CONC.      *
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C     *   CHARACTERISTICS (NEQ2).  CMSS IS THE MASS IN ALL PHASES    *
C     *   IF IV=1 VOLATILIZATION IS CONSIDERED.                      *
C     *                                                              *
C     ****************************************************************
      REAL CT(2)
      COMMON /CCHR/ CPART,CC(75,2),CO(75),TC(75),ZC(75,2)
      COMMON /CONCI/ CLAG,COINI,DLC,FCV,XSF1,XXKV,XXKW
      COMMON /COUN/ IPR(60),NUM(60),SEC(60)
      COMMON /GAEQ/ CHS(2),DO,EE,FF,GA1,GA2,GA3,GA4,HS,IGA,IP,ZGA
      COMMON /FRNT/ ISE,PF(2),PS(2),PT(2),PZ(2)
      COMMON /MATR/ ETA,OMSOR,OMSWR,SR,SWR
      COMMON /OCHR/ DLO,OLAG,SI(75,2),SO(75),TO(75),ZI(75,2)
      COMMON /POLL/ DPA,DPL,DTP,DZPMDT,DZPDDT,IAT,PKS,PVOL,QP,SPMAX,SPR,
     1              THPZ,TPB,TPE,TPR,WP(50),XKPMX,XK22
      COMMON /VAPO/ ABL,AKS,CN,CV(2),CVF(2),DAIR,XJV(2),ZV(2)
      COMMON /WTER/ IRT,SWMAX,QW,WKS
      NUM(8) = NUM(8) + 1
C
      CO = 0.
      CMSS = 0.
      IF (COINI.LE.0.) RETURN
      DT = PT(2) - PT(1)
      CT(1) = 0.
      CT(2) = 0.
      DO 100 IT = 2,1,-1
C       ***FIND NUMBER OF CHARACTERISTICS
        IF (TT.LT.TPE*1.15) THEN
          DO 20 I=2,NEQ3
            IF (ZC(I,IT).EQ.DPA) THEN
              LZ = I
              IF (TT.LT.TPE) LZ = LZ - 1
              GO TO 21
            END IF
 20       CONTINUE
 21       CONTINUE
        ELSE
          LZ = NEQ3
        END IF
C       ***FIND DEPTH OF DEEPEST & SHALLOWEST CHARACTERISTICS
        ZLOW  = ZC(LZ,IT)
        CLOW  = CC(LZ,IT)
        ZHIGH = ZC(1,IT)
C       ***DETERMINE THE CONCENTRATION
        IF (ZZ.GT.ZHIGH) GO TO 100
        IF (ZZ.LT.ZLOW) THEN
          IF (TT.GT.TPE) THEN
            GO TO 100
C         ELSE IF (ZVF.GT.DPA.AND.ZVF.LE.ZZ.AND.ZZ.LT.ZLOW) THEN
C           ***DURING VOLATILIZATION
C           SL = (CLOW-CVF)/(ZLOW-ZVF)
C           CO = CVF + (ZZ-ZVF)*SL
          ELSE IF (TT.LE.TPE) THEN
C           ***DURING LOADING
            CC1 = CPART
            IF (IGA.EQ.1) THEN
              CALL SFLUX (TT,QO)
              IF (QO.GT.0..AND.QW.GT.0.) CC1 = QO*COINI/(QO + XXKW*QW)
            END IF
            CT(IT) = CC1 + (ZZ-DPA)*(CLOW - CC1)/(ZLOW-DPA)
          ELSE
            STOP 'CONC-ZLOW'
          END IF
          IF (IZX.EQ.1) WRITE(7,1510)CT(IT),CLOW,CPART,ZZ,ZLOW
 1510     FORMAT (1X,'CONC CT(IT),CLOW,CPART,ZZ,ZLOW',5F10.3)
        ELSE
C         ***LINEAR INTERPOLATION
          CALL BINARY (ZZ,ZC(1,IT),LZ,1,IN2)
          C1 = CC(IN2,IT)
          C2 = CC(IN2+1,IT)
          Z1 = ZC(IN2,IT)
          Z2 = ZC(IN2+1,IT)
          IF (ZC(IN2+1,IT).LT.PZ(2).AND.PZ(2).LT.ZC(IN2,IT).
     1    AND.DLO.GT.0.) THEN
C           ***APPROXIMATE CONCENTRATION NEAR THE OIL FRONT
            IF (ZZ.LT.PZ(2)) THEN
              C1 = CC(IN2+1,IT)
              Z1 = PZ(2)
            ELSE
              Z2 = PZ(2)
            END IF
          END IF
          SL = (C2-C1)/(Z2-Z1)
          CT(IT) = C1 + (ZZ-Z1)*SL
        END IF
        IF (TT.EQ.PT(2)) THEN
          IF (IV.EQ.1.AND.ZZ.LT.ZV(2)) RETURN
          CO = CT(2)
          GO TO 200
        END IF
  100 CONTINUE
      DD = TT-PT(1)
      IF (TT.LT.PT(1)) STOP 'CONC-TIME'
C     ***BILINEAR INTERPOLATION ON A QUADRALATERIAL
      IF(IZX.EQ.1)WRITE(7,4330)TT,ZZ,ZC(NEQ3,2),ZC(1,1)
 4330 FORMAT(1X,'CONC TT,ZZ,ZC(NEQ3,2),ZC(1,1)',4F10.4)
      IF (TT.GT.TPE.AND.(ZZ.LT.ZC(NEQ3,2).OR.ZZ.LT.ZV(2))) THEN
        IF (ZZ.LT.ZV(1).OR.ZZ.LT.ZC(NEQ3,1)) RETURN
        C1 = CT(1)
        T1 = PT(1)
        IF (XXKV.GT.0..AND.IV.EQ.1) THEN
C         ***VOLATILE FRONT (TOP)
          ZVF = ZV(1) + DD*(ZV(2)-ZV(1))/DT
          IF (ZZ.LT.ZVF) RETURN
          C2 = CV(1) + (ZZ-ZV(1))*(CV(2)-CV(1))/(ZV(2)-ZV(1))
          T2 = PT(1) + (ZZ-ZV(1))*DT/(ZV(2)-ZV(1))
        ELSE
C         ***NONVOLATILE FRONT (TOP)
          ZF = ZC(NEQ3,1)+DD*(ZC(NEQ3,2)-ZC(NEQ3,1))/DT
          IF (ZZ.LT.ZF) RETURN
          C2 = CC(NEQ3,1)+DD*(CC(NEQ3,2)-CC(NEQ3,1))/DT
          T2 = PT(1)+(ZZ-ZC(NEQ3,1))*DT/(ZC(NEQ3,2)-ZC(NEQ3,1))
        END IF
        IF (ZZ.GT.ZC(1,1)) THEN
C         ***VERY HIGHLY SKEWED QUADS.
          ZF = ZC(1,1) + DD*(ZC(1,2)-ZC(1,1))/DT
          IF (ZZ.GT.ZF) RETURN
          C1 = CC(1,1) + DD*(CC(1,2)-CC(1,1))/DT
          T1 = PT(1) + (ZZ-ZC(1,1))/(ZC(1,2)-ZC(1,1))/DT
        END IF
        CO = C1 + (TT-T1)*(C2-C1)/(T2-T1)
      ELSE IF (ZZ.GT.ZC(1,1)) THEN
C       ***LEADING EDGE OF CONSTITUENT
        ZF = ZC(1,1) + DD*(ZC(1,2)-ZC(1,1))/DT
        IF (ZZ.GT.ZF+0.000001) RETURN
        T1 = PT(1)+(ZZ-ZC(1,1))*DT/(ZC(1,2)-ZC(1,1))
        C1 = CC(1,1)+(ZZ-ZC(1,1))*(CC(1,2)-CC(1,1))/(ZC(1,2)-ZC(1,1))
        CO = C1
        IF (ABS(TT-T1).GT.0.00001) CO = C1 + DD*(CT(2)-C1)/(TT-T1)
      ELSE
C       ***IN CENTER OF DISTRIBUTION
        CO = CT(1) + DD*(CT(2)-CT(1))/DT
      END IF
  200 CONTINUE
      CMSS = RD(SO,SW)*CO
      RETURN
      END
      SUBROUTINE OCP (TT,NEQ,A,B,IW,SUM1,SUM2)
      DIMENSION NEQ(*),CS(7),CY(7)
      COMMON /CONCI/ CLAG,COINI,DLC,FCV,XSF1,XXKV,XXKW
      COMMON /COUN/ IPR(60),NUM(60),SEC(60)
      COMMON /POLL/ DPA,DPL,DTP,DZPMDT,DZPDDT,IAT,PKS,PVOL,QP,SPMAX,SPR,
     1              THPZ,TPB,TPE,TPR,WP(50),XKPMX,XK22
      COMMON /WTER/ IRT,SWMAX,QW,WKS
      DATA CY /-.949108,-.741531,-.405845,0.,.405845,.741531,.949108/
      DATA CS /.129485,.279705,.381830,.417959,.381830,.279705,.129485/
C     ***MODIFIED GAUSS-LAGRANGE QUADRATURE FOR OIL AND CONSTITUENT
C     ***II-17-87, METHOD FROM ABRAMOWITZ AND STEGUN P. 916
      NUM(9) = NUM(9) + 1
      XC1 = (B - A)*0.5
      XC2 = (B + A)*0.5
C
C     ***FUNCTION EVALUATIONS AT GAUSS POINTS
      SUM1 = 0.
      SUM2 = 0.
      DO 10 I=1,7
        Y = CY(I)*XC1 + XC2
        CALL OIL (Y,TT,SWMAX,NEQ(2),SO)
        CALL CONC (TT,Y,SWMAX,SO,NEQ(3),CO,CM,1)
        IF (SO.LE.0.AND.CO.LE.0.) THEN
C         IF (IW.EQ.1) WRITE (9,1340) TT,Y,SO,CO*XXKW
C1340     FORMAT (1X,'OCP TT,Y,SO,CO',4F10.4)
          IF (IW.EQ.1) WRITE (9,9100)
 9100     FORMAT (/)
          RETURN
        END IF
        IF (IW.EQ.1) WRITE (9,9101) Y,SO,CO*XXKW
        SUM1 = SUM1 + SO*CS(I)
        SUM2 = SUM2 + CM*CS(I)
   10 CONTINUE
      SUM1 = SUM1*XC1
      SUM2 = SUM2*XC1
C
 9101 FORMAT (15X,F10.4,5X,3F10.4)
      RETURN
      END
      SUBROUTINE ZMASS (TH,ZH,SH,NEQ,IW,VVV,CVL)
C     *************************************************************
C     *                                                           *
C     *   ZMASS                                                   *
C     *                                                           *
C     *                                                           *
C     *   PURPOSE....THIS SUBROUTINE CREATES SATURATION AND CON-  *
C     *   CENTRATION PROFILES AT GIVEN TIMES.  THE VOLUME/AREA    *
C     *   OR MASS IN THE PROFILE IS OBTAINED BY GAUSS-LAGRANGE    *
C     *   QUADRATURE OF THE PROFILE (ROUTINE GLQ OR OCP).         *
C     *                                                           *
C     *   INPUT ARGUMENTS.......................................  *
C     *   TH      = TIME                                          *
C     *   ZH      = MAXIMUM DEPTH OF OIL                          *
C     *   SH      = OIL SATURATION AT ZH                          *
C     *   NEQ     = ARRAY CONTAINING NUMBER OF EQUATIONS          *
C     *   IW      = WRITE RESULTS INTO FILE PROF IF IW=1          *
C     *                                                           *
C     *   OUTPUT ARGUMENTS......................................  *
C     *   VVV     = VOLUME/AREA OF OIL                            *
C     *   CVL     = MASS/AREA OF CONSTITUENT                      *
C     *                                                           *
C     *                                                           *
C     *   AUTHOR  JIM WEAVER                                      *
C     *           THE UNIVERSITY OF TEXAS AT AUSTIN               *
C     *                                                           *
C     *   SINGLE PRECISION, ANSI STD. X3.9-1978 FORTRAN 77        *
C     *   REQUIRED ROUTINES...CONC,OIL,OCP,GLQ                    *
C     *   X-21-87, VII-18-88                                      *
C     *                                                           *
C     *************************************************************
      DIMENSION NEQ(*),ZX(10)
      CHARACTER NT*15
      COMMON /CCHR/ CPART,CC(75,2),C0(75),TC(75),ZC(75,2)
      COMMON /CONCI/ CLAG,COINI,DLC,FCV,XSF1,XXKV,XXKW
      COMMON /COUN/ IPR(60),NUM(60),SEC(60)
      COMMON /FRNT/ ISE,PF(2),PS(2),PT(2),PZ(2)
      COMMON /GAEQ/ CHS(2),DO,EE,FF,GA1,GA2,GA3,GA4,HS,IGA,IP,ZGA
      COMMON /MATR/ ETA,OMSOR,OMSWR,SR,SWR
      COMMON /NAME/ NT(15)
      COMMON /OCHR/ DLO,OLAG,SI(75,2),S0(75),T0(75),ZI(75,2)
      COMMON /POLL/ DPA,DPL,DTP,DZPMDT,DZPDDT,IAT,PKS,PVOL,QP,SPMAX,SPR,
     1              THPZ,TPB,TPE,TPR,WP(50),XKPMX,XK22
      COMMON /VAPO/ ABL,AKS,CN,CV(2),CVF(2),DAIR,XJV(2),ZV(2)
      COMMON /WTER/ IRT,SWMAX,QW,WKS
      NUM(10) = NUM(10) + 1
      VVV = 0.
      NN = 1
      DO 5 II=1,10
        ZX(II) = 0.
 5    CONTINUE
C
      IF (TH.GT.TPE) THEN
        SS = SPR
        IF (DLO.GT.0..AND.TH.GT.OLAG)
     1  SS = SPR*EXP( - DLO*(TH-OLAG))
      ELSE
```

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        SS = SPMAX
      END IF
C     ***DIVIDE THE PROFILE INTO SUBSECTIONS FOR INTEGRATION
C     ***OIL LOCATIONS
      NN = NN + 1
      ZX(NN) = ZH
      IF (SH.GE.SPMAX.AND.DLO.LE.0.) THEN
        T1 = TPE
        IF (CHS(2).GT.0..AND.IGA.EQ.1) T1 = 2.*TH
        IF (TH.GT.T1) THEN
          NN = NN + 1
          ZD = DPA + (TH-TPE)*DZPDDT
          ZX(NN) = ZD
          NN = NN + 1
          ZX(NN) = DPA + 0.3333*(ZD-DPA)
          NN = NN + 1
          ZX(NN) = DPA + 0.6666*(ZD-DPA)
        END IF
      ELSE IF (DLO.GT.0.) THEN
        IF (TH.GT.TPE.AND.NEQ(2).GT.41.AND.ZI(41,2).GT.DPA
     1  .AND.ZH.GT.ZI(41,2))THEN
          NN = NN + 1
          ZX(NN) = ZI(41,2)
          NN = NN + 1
          ZX(NN) = DPA + (ZI(41,2)-DPA)*0.5
        END IF
      END IF
C
      IF (COINI.GT.0.) THEN
C       ***CONSTITUENT PROFILE LOCATIONS
        NN = NN + 1
        ZX(NN) = ZC(1,2)
        ZCT = ZC(NEQ(3),2)
        ZCV = ZV(2)
        IF (ZCV.GT.ZCT) ZCT = ZCV
        NN = NN + 1
        ZX(NN) = ZCT
      END IF
C
C     ***ELIMINATE ZEROS
      I = 1
      NX = NN
 20   CONTINUE
        I = I + 1
        IF (I.EQ.51) STOP 'ZMASS ELIMINATE ZEROS'
        IF (ZX(I).LE.0.) THEN
          NX = NX - 1
          DO 15  J=I,NX
            ZX(J) = ZX(J+1)
 15       CONTINUE
          I = I - 1
        END IF
      IF (I.LT.NX) GO TO 20
C
C     ***SORT THE DEPTHS
      DO 30 J=1,100
        IH = 0
        DO 25  I=1,NX-1
          IF (ZX(I).GT.ZX(I+1)) THEN
            IH = 1
            ZTEMP = ZX(I)
            ZX(I) = ZX(I+1)
            ZX(I+1) = ZTEMP
          END IF
 25     CONTINUE
        IF (IH.EQ.0) GO TO 31
 30   CONTINUE
      STOP 'ZMASS  SORTING FAILURE'
 31   CONTINUE
      NN = NX
C
      CVL = 0.
      CALL CONC (TH,DPA,SWMAX,SS,NEQ(3),CCC,CXX,1)
      IF (IW.EQ.1) THEN
        WRITE (9,9100) TH,(NT(II),II=1,15)
        WRITE (9,9106)
        WRITE (9,9107) DPA,SS,CCC*XXKW
      END IF
C
C     ***OIL AND CONSTITUENT PROFILE
      DO 10 I=1,NN-1
        OVOL = 0.
        CVOL = 0.
        IF (IW.EQ.1) THEN
          CALL OIL (ZX(I)*1.000001,TH,SWMAX,NEQ(2),SSS)
          CALL CONC (TH,ZX(I)*1.000001,SWMAX,SSS,NEQ(3),CCC,CXX,1)
          WRITE (9,9107) ZX(I),SSS,CCC*XXKW
        END IF
        CALL OCP (TH,NEQ,ZX(I),ZX(I+1),IW,OVOL,CVOL)
        IF (IW.EQ.1) THEN
          CALL OIL (ZX(I+1)*.999999,TH,SWMAX,NEQ(2),SSS)
          CALL CONC (TH,ZX(I+1)*.999999,SWMAX,SSS,NEQ(3),CCC,CXX,1)
          WRITE (9,9107) ZX(I+1),SSS,CCC*XXKW
        END IF
        VVV = VVV + OVOL*ETA
        CVL = CVL + CVOL*FCV
 10   CONTINUE
      IF (IW.EQ.1) WRITE (9,9115) VVV,CVL
C
      RETURN
 9100 FORMAT (1H1/10X,'SATURATION AND CONCENTRATION PROFILE AT ',F10.4/
     2        10X,50(1H*)/
     3        3(10X,5A10/)/)
 9106 FORMAT (15X,3X,'DEPTH',2X,5X,4X,'SAT.',2X,'CONC.(WATER)'/
     2        15X,35(1H=))
 9107 FORMAT (15X,F10.4,5X,2F10.4,'*')
 9110 FORMAT (15X,F10.4,5X,F10.4//
     1        10X,'VOLUME/AREA ',F10.4///)
 9115 FORMAT (//10X,'OIL VOLUME/AREA ',F10.4,' CONSTITUENT MASS/AREA ',
     1            F10.4)
      END
      SUBROUTINE OIL (ZZ,TT,SW,NEQ2,SO)
C     ***************************************************************
C     *                                                             *
C     *  OIL                                                        *
```

```
C     *                                                            *
C     *  FOR TIME TT, (BETWEEN PT(1) AND PT(2)), OIL FINDS THE OIL *
C     *  SATURATION AT DEPTH ZZ GIVEN THE WATER SATURATION SW      *
C     *                                                            *
C     **************************************************************
      REAL SS(2)
      COMMON /COUN/ IPR(60),NUM(60),SEC(60)
      COMMON /FRNT/ ISE,PF(2),PS(2),PT(2),PZ(2)
      COMMON /GAEQ/ CHS(2),DO,EE,FF,GA1,GA2,GA3,GA4,HS,IGA,IP,ZGA
      COMMON /MATR/ ETA,OMSOR,OMSWR,SR,SWR
      COMMON /OCHR/ DLO,OLAG,SI(75,2),SO(75),TO(75),ZI(75,2)
      COMMON /POLL/ DPA,DPL,DTP,DZPMDT,DZPDDT,IAT,PKS,PVOL,QP,SPMAX,SPR,
     1              THPZ,TPB,TPE,TPR,WP(50),XKPMX,XK22
      COMMON /WTER/ IRT,SWMAX,QW,WKS
      NUM(11) = NUM(11) + 1
      SO = 0.
C     ***IMMOBILIZED OIL LAYERS
      IF (IAT.EQ.2.AND.QP.LE.0.) THEN
        IF (DPA.LE.ZZ.AND.ZZ.LE.DPL) THEN
          XXX = 1.
          IF (TT.GT.OLAG) XXX = EXP(-DLO*(TT-OLAG))
          SO = SPMAX*XXX
        END IF
        RETURN
      END IF
      IF (ZZ.LT.DPA) RETURN
      DT = PT(2) - PT(1)
      ZF = PZ(2)
      IF (TT.LT.PT(2).AND.PT(2).NE.PT(1)) THEN
        IF (TT.LT.PT(1)) STOP 'BAD-OIL'
        ZF = PZ(1)+(TT-PT(1))*(PZ(2)-PZ(1))/DT
      END IF
      IF (ZZ.GT.ZF) RETURN
C
C     ***MOBILE OILS
      IF (DLO.EQ.0.) THEN
        Z22 = DPA + (TT - TPE)*DZPDDT
        IHS = 0
        IF (IGA.EQ.1.AND.IP.EQ.1.AND.CHS(2).GT.0.) Z22 = DPA
        IF (ZZ.GE.Z22.AND.((ZZ.LT.ZF.OR.ABS(ZZ-ZF).LE.1.E-5)
     1  .OR.(IP.EQ.1.AND.CHS(2).GT.0..AND.ZZ.LE.ZF))) THEN
          SO = SPMAX
        ELSE IF (ZZ.LE.ZF) THEN
          SL = (ZZ-DPA)/(TT-TPE)
          CALL INQUAD (WP,50,SPR,1.-SWMAX,SL*ETA,SO)
        END IF
      ELSE
C       ***DEGRADING OILS
        DO 100 IT=2,1,-1
          ZF = PZ(IT)
          IF (PT(1).LE.TPE) THEN
            LZ = NEQ2
            DO 20 I=NEQ2-1,1,-1
              IF (ZI(I,IT).LE.DPA) THEN
                LZ = I + 1
                GO TO 21
              END IF
 20         CONTINUE
 21           CONTINUE
          ELSE
            LZ = 1
          END IF
          IF (ZZ.LE.ZI(LZ,IT).AND.TT.LE.TPE) THEN
            SL = 0.
            IF (ZI(LZ,IT).GT.DPA) SL = (SI(LZ,IT)-SPMAX)/
     1      (ZI(LZ,IT)-DPA)
            SS(IT) = SPMAX + SL*(ZZ-DPA)
          ELSE
            IX = 0
            CALL BINARY (ZZ,ZI(LZ-1,IT),NEQ2-LZ+1,1,IX)
            IF (LZ.GT.1) IX = LZ + IX - 1
            SL = (SI(IX+1,IT)-SI(IX,IT))/(ZI(IX+1,IT)-ZI(IX,IT))
            SS(IT) = SI(IX,IT) + (ZZ-ZI(IX,IT))*SL
          END IF
          IF (TT.EQ.PT(IT)) THEN
            IF (DPA.LE.ZZ.AND.ZZ.LE.ZF) SO = SS(IT)
            RETURN
          END IF
 100    CONTINUE
        SL = (SS(2)-SS(1))/DT
        SO = SS(1) + (TT-PT(1))*SL
      END IF
      RETURN
      END
      SUBROUTINE HIST (ZZ,Z1,ND,NEQ,TT)
      DIMENSION NEQ(*),SC(15),TZ(10),ZZ(ND,*),Z1(ND,*)
      COMMON /CCHR/ CPART,CC(75,2),C0(75),TC(75),ZC(75,2)
      COMMON /COUN/ IPR(60),NUM(60),SEC(60)
      COMMON /CONCI/ CLAG,COINI,DLC,FCV,XSF1,XXKV,XXKW
      COMMON /FRNT/ ISE,PF(2),PS(2),PT(2),PZ(2)
      COMMON /GAEQ/ CHS(2),DO,EE,FF,GA1,GA2,GA3,GA4,HS,IGA,IP,ZGA
      COMMON /HIPR/ IHIST,NTIMES,PR(10),NZS,HI(5)
      COMMON /POLL/ DPA,DPL,DTP,DZPMDT,DZPDDT,IAT,PKS,PVOL,QP,SPMAX,SPR,
     1              THPZ,TPB,TPE,TPR,WP(50),XKPMX,XK22
      COMMON /WTER/ IRT,SWMAX,QW,WKS
C
C     ***PRODUCES HISTORIES IN FILE HIST (10)
      NUM(12) = NUM(12) + 1
      II = 1
      TZ(1) = TT
      I1 = 1
      DO 10 I=1,15
         SC(I) = 0.
 10   CONTINUE
C
C     ***CHECK FOR OIL OR CONSTITUENT FIRST REACHING THE OUTPUT DEPTHS
C     ***REASSIGN OUTPUT TIMES IF SO
      IF (COINI.GT.0.) THEN
        DO 15 I=1,NZS
          IF (ZC(1,1).LE.HI(I).AND.HI(I).LT.ZC(1,2)) THEN
            I1 = I1 + 1
            SL = (PT(2)-PT(1))/(ZC(1,2)-ZC(1,1))
            TZ(I1) = PT(1)+(HI(I)-ZC(1,1))*SL
            II = I1
          END IF
C
```

```
C         ***CONSTITUENT PASSING OUTPUT DEPTHS
          IF (ZC(NEQ(3),1).LE.HI(I).AND.HI(I).LT.ZC(NEQ(3),2)) THEN
            I1 = I1 + 1
            SL = (PT(2)-PT(1))/(ZC(NEQ(3),2)-ZC(NEQ(3),1))
            TZ(I1) = PT(1)+(HI(I)-ZC(NEQ(3),1))*SL
            II = I1
          END IF
 15     CONTINUE
      END IF
C     WRITE (10,1305) TZ(1),TT
C
C     ***OIL FIRST REACHING DEPTHS
      DO 16 I=1,NZS
        IF (PZ(1).LE.HI(I).AND.HI(I).LT.PZ(2)) THEN
          I1 = I1 + 1
          SL = (PT(2)-PT(1))/(PZ(2)-PZ(1))
          TZ(I1) = PT(1)+(HI(I)-PZ(1))*SL
          II = I1
        END IF
 16   CONTINUE
C
C     ***SORT THE OUTPUT TIMES
C     WRITE (10,1305) TZ(1),TT
      DO 18 L=1,II
        J = 0
        DO 17 M=1,II-1
          IF (TZ(M+1).LT.TZ(M)) THEN
            TEMP = TZ(M)
            TZ(M) = TZ(M+1)
            TZ(M+1) = TEMP
            J = 1
          END IF
 17     CONTINUE
        IF (J.EQ.0) GO TO 19
 18   CONTINUE
 19   CONTINUE
C
C     ***COLLECT INFORMATION FOR EACH OUTPUT TIME
C     WRITE (10,1305) TZ(1),TT
      DO 30  L=1,II
        DO 20 I=1,NZS
          J = 3*I-2
          CALL OIL (HI(I),TZ(L),SWMAX,NEQ(2),SC(J))
          SC(J+1) = 0.
          IF (IGA.EQ.1..AND.SC(J).GE.SPMAX) THEN
            SC(J+1) = PF(2)
            IF (TZ(L).LT.PT(2)) THEN
              IF (TZ(L).LT.PT(1)) STOP 'HIST-TIME'
              SL = (PF(2)-PF(1))/(PT(2)-PT(1))
              SC(J+1) = PF(1) + (TZ(L)-PT(1))*SL
            END IF
          ELSE IF (SC(J).GT.0.) THEN
            CALL PKE (0,SC(J),0,SWMAX,SC(J+1),0.,0)
          END IF
          SC(J+2) = 0.
          IF (COINI.GT.0.) CALL CONC (TZ(L),HI(I),SWMAX,SC(J),NEQ(3),
     1    SC(J+2),X,1)
          SC(J+2)= SC(J+2)*XXKW
 20     CONTINUE
        IX = 0
        DO 25 IJ = 1,NZS*3
          IF (SC(IJ).GT.0.) IX = 1
 25     CONTINUE
        IF (IX.EQ.1) WRITE (10,9201) TZ(L),(SC(J),J=1,3*NZS)
 30   CONTINUE
 9201 FORMAT (1X,F9.4,3(3F10.4))
      RETURN
      END
      SUBROUTINE SFLUX (TT,QO)
      COMMON /COUN/ IPR(60),NUM(60),SEC(60)
      COMMON /FRNT/ ISE,PF(2),PS(2),PT(2),PZ(2)
      COMMON /GAEQ/ CHS(2),DO,EE,FF,GA1,GA2,GA3,GA4,HS,IGA,IP,ZGA
      COMMON /POLL/ DPA,DPL,DTP,DZPMDT,DZPDDT,IAT,PKS,PVOL,QP,SPMAX,SPR,
     1              THPZ,TPB,TPE,TPR,WP(50),XKPMX,XK22
C     ***RETURNS THE FLUX AT THE SURFACE TO CORRECT SOME CONCENTRATIONS
      NUM(13) = NUM(13) + 1
      QO = 0.
      IF (IGA.EQ.0) THEN
        IF (TT.LE.TPE) QO = QP
      ELSE
        IF (CHS(1).GT.0..OR.(TT.LE.TPE)) THEN
          QO = PF(2)
          IF (PT(1).LE.TT.AND.TT.LT.PT(2)) THEN
            SL = (PF(2)-PF(1))/(PT(2)-PT(1))
            QO = PF(1) + (TT-PT(1))*SL
          END IF
        END IF
      END IF
      RETURN
      END
      SUBROUTINE INPUT
C     **************************************************************
C     *
C     *  REQUIRED INPUT DATA
C     *      (SEE EXPLANATORY NOTES BELOW)
C     *
C     *  CARD 1-3...RUN TITLE...(5A10/5A10/5A10).....................
C     *  NT(15)     RUN TITLE  3 LINES OF 50 CHARACTERS EACH
C     *
C     *  CARD 4.....MATRIX PROPERTIES...(5F10.4).....................
C     *  WKS        SATURATED HYDRAULIC CONDUCTIVITY (WATER)
C     *  XLAMB      BROOKS AND COREY'S LAMBDA
C     *  ETA        POROSITY
C     *  RHOS       BULK DENSITY OF MATRIX
C     *  SWR        RESIDUAL WATER SATURATION
C     *
C     *  CARD 5.....WATER PROPERTIES...(2F10.4,I10,F10.4)............
C     *  WMU        DYNAMIC VISCOSITY OF WATER
C     *  WRHO       DENSITY OF WATER
C     *  IRT        RAINFALL INPUT TYPE:  1=FLUX SPECIFIED
C     *                                   2=SATURATION SPECIFIED
C     *                                   3=CONSTANT HEAD
C     *  QW/SWMAX   CONSTANT WATER FLUX OR SATURATION
C     *
C     *  CARD 6.....OIL CHARACTERISTICS...(4F10.4,I10)...............
C     *  PMU        DYNAMIC VISCOSITY OF OIL
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C     *  PRHO       OIL DENSITY
C     *  SPR        RESIDUAL (TRAPPED) OIL SATURATION
C     *  HLO        OIL HALF LIFE (=0. IF NON-DEGRADIBLE)
C     *  OLAG       ACCLIMATION TIME FOR BIODEGRADATION TO BEGIN
C     *  IAT        OIL INPUT TYPE  1=FLUX SPECIFIED
C     *                             2=VOLUME/AREA SPECIFIED
C     *  CARD 7.....(FOR IAT=1)...OIL FLUX...(4F10.4,I10,F10.4)......
C     *  QP         OIL FLUX (VOLUME/AREA/TIME)
C     *  TPB        OIL EVENT BEGINNING TIME
C     *  TPE        OIL EVENT ENDING TIME
C     *  DPA        DEPTH AT WHICH POLLUTANTS ARE APPLIED
C     *  IP         PONDING TYPE  0=EXCESS OIL RUNS OFF SURFACE
C     *                           1=VARIABLE (SEE NOTE 4.)
C     *                           3=CONSTANT
C     *  HS         CONSTANT HEAD FOR IP=3 CASES
C     *
C     *  CARD 7.....(FOR IAT = 2)...OIL VOLUME...(3F10.4)............
C     *  PVOL       OIL VOLUME/AREA INCORPORATED INTO THE SOIL
C     *  DPA        DEPTH AT WHICH POLLUTANTS ARE APPLIED
C     *  DPL        LOWER DEPTH OF INITIALLY POLLUTED ZONE
C     *
C     *  CARD 7.....(FOR IAT = 3)...CONSTANT HEAD..(4F10.4,I10,F10.4)
C     *             ***SAME AS FOR IAT=1, EXCEPT QP IS MEANINGLESS
C     *
C     *  CARD 8.....DISSOLVED CONSTITUENT...(6F10.4).................
C     *  COINI      INITIAL CONCENTRATION IN OIL (SEE NOTE 5.)
C     *  FCV        (SEE NOTE 5.)
C     *  HLC        CONSTITUENT HALF LIFE (=0. IF NONDEGRADING)
C     *  CLAG       ACCLIMATION TIME FOR BIODEGRADATION TO BEGIN
C     *
C     *  CARD 8.....DISSOLVED CONSTITUENT...(6F10.4).................
C     *  PARTITIONING COEFFICIENTS:
C     *  XXKO       OIL/WATER         (C0 = XXKW*CW)
C     *  XXKV       DIMENSIONLESS HENRY'S LAW COEFF.
C     *  XKOC       SOLID/ORGANIC CARBON
C     *
C     *  CARD 10....VOLATILIZATION MODEL...(6F10.4)..................
C     *  DAIR       DIFFUSION COEFFICIENT FOR CONSTITUENT IN AIR
C     *  DWV        DIFFUSTION COEFFICENT FOR WATER VAPOR
C     *  EVAP       WATER EVAPORATION RATE (VOL./AREA/TIME)
C     *  TEMP       TEMPERATURE IN DEGREES C
C     *  RH         RELATIVE HUMIDITY
C     *  XCF        CONVERSION FACTOR TO GR/CC (SEE NOTE 2)
C     *
C     *  CARD 11....SIMULATION PARAMETERS...(3F10.4)................
C     *  TM         SIMULATION ENDING TIME
C     *  DM         MAXIMUM SOLUTION TIME STEP
C     *  DTPR       MINIMUM TIME BETWEEN PRINTED TIME STEPS AND
C     *             MASS BALANCE CHECKS
C     *
C     *  CARD 12....PROFILES AND HISTORIES...(2I5).................
C     *  NTIMES     NUMBER OF PROFILES DESIRED (UP TO 10)
C     *  NZS        NUMBER OF HISTORIES DESIRED (UP TO 3)
C     *
C     *  CARD 13....(5F10.4/5F10.4)..................................
C     *  PR(NTIMES) PROFILE TIMES
C     *
C     *  LAST CARD..(3F10.4)..........................................
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C     *  HI(NZS)    HISTORY DEPTHS
C     *
C     *
C     *  NOTES:
C     *  1.   ALL VARIABLE NAMES ARE IN ACCORDANCE WITH FORTRAN NAM-
C     *       ING CONVENTIONS--NAMES BEGINNING WITH I THROUGH M ARE
C     *       INTEGERS, ALL OTHERS ARE REALS.
C     *  2.   WITH THE FOLLOWING EXCEPTIONS, ALL INPUT PARAMETERS MUST
C     *       BE GIVEN IN A CONSISTENT SYSTEM OF UNITS.
C     *       -THE TEMPERATURE MUST BE GIVEN IN DEGREES C
C     *       -THE CONVERSION FACTOR FROM THE CONSISTENT SET OF UNITS TO
C     *        GR/CC MUST BE GIVEN (PART OF THE VOLATILIZATION MODEL
C     *        USES AN EMPIRICAL FORMULA FOR VAPOR PRESSURE/DENSITY).
C     *  3.   ZEROS SHOULD BE READ IN FIELDS PERTAINING TO UNUSED VALUES
C     *  4.   VARIABLE SURFACE PONDING IS SUPPORTED ONLY FOR CASES WITH
C     *       NO DISSOLVED CONSTITUENT PRESENT
C     *  5.   THE CONCENTRATION OF THE DISSOLVED CONSTITUENT CAN BE READ
C     *       IN IN ANY DESIRED UNITS (EG. MG/L).  A CONVERSION TO THE
C     *       CONSISTENT VOLUME UNIT MUST BE READ IN VARIABLE FCV IN
C     *       ORDER FOR THE CALCULATED MASS BALANCES TO BE CORRECT
C     *       E.G.  CONCENTRATION IN MG/L, C-G-S UNITS, FCV = 0.0001
C     *       OUTPUT CONCENTRATIONS IN MG/L, MASS BALANCE IN MG/CM2
C     *
C     ***************************************************************
      CHARACTER NT*15
      COMMON /COUN/ IPR(60),NUM(60),SEC(60)
      COMMON /CONCI/ CLAG,COINI,DLC,FCV,XSF1,XXKV,XXKW
      COMMON /GAEQ/ CHS(2),DO,EE,FF,GA1,GA2,GA3,GA4,HS,IGA,IP,ZGA
      COMMON /HIPR/ IHIST,NTIMES,PR(10),NZS,HI(5)
      COMMON /MATR/ ETA,OMSOR,OMSWR,SR,SWR
      COMMON /NAME/ NT(15)
      COMMON /OCHR/ DLO,OLAG,SI(75,2),SO(75),TO(75),ZI(75,2)
      COMMON /POLL/ DPA,DPL,DTP,DZPMDT,DZPDDT,IAT,PKS,PVOL,QP,SPMAX,SPR,
     1              THPZ,TPB,TPE,TPR,WP(50),XKPMX,XK22
      COMMON /RLTV/ KRF,XLAMB,A2A,A3A,A4A,A5A,A6A
      COMMON /SIMU/ DM,DTPR,TM
      COMMON /VAPO/ ABL,AKS,CN,CV(2),CVF(2),DAIR,XJV(2),ZV(2)
      COMMON /WTER/ IRT,SWMAX,QW,WKS
      EXTERNAL SLOPE
      NUM(14) = NUM(14) + 1
C
C     ***READ THE INPUT DATA
      OPEN (5,FILE='INPUT.KOP',STATUS='OLD')
      OPEN (6,FILE='OUTPUT.KOP',STATUS='UNKNOWN')
      OPEN (7,FILE='RES',STATUS='UNKNOWN')
      OPEN (8,FILE='PLOT',STATUS='UNKNOWN')
      OPEN (9,FILE='PROF',STATUS='UNKNOWN')
      OPEN (10,FILE='HIST',STATUS='UNKNOWN')
      DO 10 I=5,10
        REWIND I
 10   CONTINUE
C     ***RUN TITLE
      READ (5,9000) (NT(I),I=1,15)
      WRITE (6,9100) (NT(I),I=1,15)
C     ***CONSTANTS AND MATRIX PROPERTIES
      READ (5,*) WKS,XLAMB,ETA,RHOS,SWR
      WRITE (6,9101) WKS,XLAMB,ETA,RHOS,SWR
C     ***WATER EVENT CHARACTERISTICS
```

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      READ (5,*) WMU,WRHO,IRT,QW
      IF (IRT.EQ.2) SWMAX = QW
      WRITE (6,9102) WMU,WRHO,IRT,QW
C     ***POLLUTANT CHARACTERISTICS
      READ (5,*) PMU,PRHO,SPR,HLO,OLAG,IAT
      WRITE (6,9103) PMU,PRHO,SPR,HLO,OLAG,IAT
      IF (IAT.EQ.1.OR.IAT.EQ.3) THEN
C       ***POLLUTANT FLUX EVENT CHARACTERISTICS
        READ (5,*) QP,TPB,TPE,DPA,IP,HS
        WRITE (6,9104) QP,TPB,TPE,DPA,IP,HS
      ELSE IF (IAT.EQ.2) THEN
C       ***POLLUTANT VOLUME EVENT CHARACTERISTICS
        READ (5,*) PVOL,DPA,DPL
        WRITE (6,9105) PVOL,DPA,DPL
      END IF
      OLAG = TPB+OLAG
C     ***DISSOLVED CONSTITUENT PARAMETERS
      READ (5,*) COINI,FCV,HLC,CLAG
      READ (5,*) XXKO,XXKV,XKOC
      WRITE (6,9106) COINI,FCV,HLC,CLAG
      WRITE (6,9107) XXKO,XXKV,XKOC
      XXKS = XKOC/WRHO
      CLAG = TPB+CLAG
C     ***VOLATILIZATION PARAMETERS
      READ (5,*) DAIR,DWV,EVAP,TEMP,RH,XCF
      WRITE (6,9108) DAIR,DWV,EVAP,TEMP,RH,XCF
C     ***SIMULATION PARAMETERS
      READ (5,*) TM,DM,DTPR
      DM = 1.1*DM
      WRITE (6,9109) TM,DM,DTPR
C     ***OUTPUT PROFILE TIMES AND HISTORY DEPTHS
      READ (5,*) NTIMES,NZS
      IF (NTIMES.GT.10.OR.NZS.GT.3) STOP 'INPUT PROFILE/HISTORY'
      READ (5,*) (PR(I),I=1,NTIMES)
      WRITE (6,9110) NTIMES,(PR(I),I=1,NTIMES)
C     ***SORT THE OUTPUT TIMES
      DO 15 J=1,NTIMES
        IH = 0
        DO 14 I=1,NTIMES-1
          IF (PR(I).GT.PR(I+1)) THEN
            IH = 1
            PTEM = PR(I)
            PR(I) = PR(I+1)
            PR(I+1) = PTEM
          END IF
 14     CONTINUE
        IF (IH.EQ.0) GO TO 16
 15   CONTINUE
 16   CONTINUE
      READ (5,*) (HI(I),I=1,NZS)
      WRITE (6,9111) NZS,(HI(I),I=1,NZS)
      WRITE (6,9190)
C     ***END OF INPUT DATA
C
      SR    = SPR + SWR
      OMSWR = 1. - SWR
      OMSOR = 1. - SPR
      PKS   = WKS*PRHO*WMU/WRHO/PMU
      IF (XXKO.EQ.0.) STOP 'INPUT:  XXKW CANNOT BE ZERO'
      XXKW  = 1./XXKO
      XXKV  = XXKV/XXKO
      XSF1  = RHOS*XXKS/ETA/XXKO
      IHIST = 0
      DO 20 I=1,NZS
        IF (HI(I).GE.DPA) IHIST = 1
 20   CONTINUE
      IF (IHIST.EQ.0) WRITE (6,9170)
      CALL KRSET
      IF (IAT.NE.2) THEN
        DPL = DPA
        DTP   = TPE - TPB
        PVOL  = DTP*QP
      END IF
      WRITE (6,9180) PKS
      IF (XXKV.GT.0.) THEN
C       ***CALCULATION OF ATMOSPHERIC BOUNDARY LAYER
C       ***LINSLEY, KOHLER & PAULHUS, 1975, PG. 35
C       ***SATURATION VAPOR PRESSURE FORMULA PG. 35
        ES = 33.8639*((0.00738*TEMP + 0.8072)**8 - .000019*
     1  ABS(1.8*TEMP+ 48.) + 0.001316)
        RWV = ES/(TEMP+273)/2876.*.622
        ABL = DWV*RWV*XCF*(1.-RH)/2./EVAP/WRHO
        WRITE (6,9184) ABL
      END IF
      IF (HLO.NE.0.) THEN
        DLO  = - ALOG(0.5)/HLO
        WRITE (6,9181) DLO
      END IF
      IF (HLC.NE.0.) THEN
        DLC = - ALOG(0.5)/HLC
        WRITE (6,9182) DLC
      END IF
      RETURN
C
 9000 FORMAT (5A10/5A10/5A10)
 9001 FORMAT (7F10.4)
 9002 FORMAT (4F10.4,I10,F10.4)
 9003 FORMAT (5F10.4,I10)
 9004 FORMAT (2F10.4,I10,F10.4)
 9005 FORMAT (5F10.4)
 9007 FORMAT (10I5)
 9100 FORMAT (1H1/10X,50(1H*)/
     1        10X,'KOPT            KINEMATIC OILY POLLUTANT TRANSPORT'/
     2        10X,50(1H*)/
     3        3(10X,5A10/)//
     4        15X,10HINPUT DATA/
     5        15X,10(1H=)/)
 9101 FORMAT (15X,30HCONSTANTS & MATRIX PROPERTIES.,10(1H.)/
     1        15X,30HSAT. HYDRAULIC CONDUCTIVITY = ,F10.4/
     2        15X,30HPORE SIZE DIST. INDEX       = ,F10.4/
     3        15X,30HPOROSITY                    = ,F10.4/
     4        15X,30HBULK DENSITY                = ,F10.4/
     5        15X,30HRESIDUAL WATER SATURATION   = ,F10.4/)
 9102 FORMAT (15X,30HWATER EVENT CHARACTERISTICS...,10(1H.)/
     1        15X,30HDYNAMIC VISCOSITY           = ,F10.4/
     2        15X,30HDENSITY                     = ,F10.4/
     3       15X,30HRAIN TYPE : 1-FLUX 2-SAT.   = ,I10/
     4       15X,30HWATER FLUX OR SATURATION    = ,F10.4/)
 9103 FORMAT (15X,35HPOLLUTANT EVENT CHARACTERISTICS....,5(1H.)/
     1       15X,30HDYNAMIC VISCOSITY           = ,F10.4/
     2       15X,30HDENSITY                     = ,F10.4/
     3       15X,30HRESIDUAL OIL SATURATION     = ,F10.4/
     4       15X,30HOIL HALF LIFE               = ,F10.4/
     5       15X,30HACCLIMATION TIME            = ,F10.4/
     6       15X,30HOIL LOADING TYPE            = ,I10)
 9104 FORMAT (15X,30HFLUX LOADING RATE           = ,F10.4/
     1       15X,30HBEGINNING TIME              = ,F10.4/
     2       15X,30HENDING TIME                 = ,F10.4/
     3       15X,30HDEPTH OF APPLICATION        = ,F10.4/
     4       15X,30HTYPE OF SURFACE PONDING     = ,I10/
     5       15X,30HDEPTH OF PONDING            = ,F10.4/)
 9105 FORMAT (15X,30HOIL VOLUME/AREA             = ,F10.4/
     1       15X,30HDEPTH: TOP OF OIL LAYER     = ,F10.4/
     2       15X,30HDEPTH: BOTTOM OF OIL LAYER  = ,F10.4/)
 9106 FORMAT (15X,32HDISSOLVED CONSTITUENT PARAMETERS,8(1H.)/
     1       15X,30HINITIAL CONC. IN OIL        = ,F10.4/
     2       15X,30HCONVERSION TO CONST. UNITS  = ,F10.4/
     3       15X,30HCONSTITUENT HALF LIFE       = ,F10.4/
     4       15X,30HACCLIMATION TIME            = ,F10.4)
 9107 FORMAT (15X,30HOIL/WATER PARTITION COEF.   = ,F10.4/
     1       15X,30HDIMENSIONLESS HENRY'S LAW   = ,F10.4/
     2       15X,30HSOIL/WATER PARTITION COEF.  = ,F10.4/)
 9108 FORMAT (15X,31HVOLATILIZATION MODEL PARAMETERS,9(1H.)/
     1       15X,30HAIR-GAS  DIFFUSION COEFF.   = ,F10.4/
     2       15X,30HAIR-WATER VAPOR DIFF. COEFF.= ,F10.4/
     3       15X,30HEVAPORATION RATE            = ,F10.4/
     4       15X,30HTEMPERATURE DEG. C          = ,F10.4/
     5       15X,30HRELATIVE HUMIDITY           = ,F10.4/
     6       15X,30HCONVERSION TO GR/CC         = ,F10.4/)
 9109 FORMAT (15X,30HSIMULATION PARAMETERS.........,10(1H.)/
     1       15X,30HSIMULATION ENDING TIME      = ,F10.4/
     2       15X,30HMAXIMUM RKF TIME STEP       = ,F10.4/
     3       15X,30HMIN. TIME BETWEEN PRINTING  = ,F10.4/)
 9110 FORMAT (15X,30HPROFILES AND HISTORIES........,10(1H.)/
     1       15X,30HNUMBER OF PROFILES          = ,I10/
     2       15X,30HAT TIMES:                     ,/
     3       2(15X,5F6.2/))
 9111 FORMAT (15X,30HNUMBER OF HISTORIES         = ,I10/
     1       15X,30HAT DEPTHS:                    ,/
     2       15X,5F6.2/)
 9160 FORMAT (15X,30HRELATIVE VAPOR DENSITY      = ,F10.4)
 9170 FORMAT (15X,'***HISTORY DEPTHS ABOVE APPLICATION DEPTH***')
 9180 FORMAT (15X,21HCALCULATED PARAMETERS,19(1H.)/
     1       15X,30HSAT. OIL   CONDUCTIVITY     = ,F10.4)
 9181 FORMAT (15X,30HOIL DECAY RATE              = ,F10.4)
 9182 FORMAT (15X,30HCONSTITUENT DECAY RATE      = ,F10.4)
 9184 FORMAT (15X,30HATM. BNDRY. LAYER THICKNESS = ,F10.4)
 9190 FORMAT (/15X,'***END OF INPUT DATA***'/)
      END
      SUBROUTINE START (NEQ,ZZ,ND)
      DIMENSION NEQ(*),ZZ(ND,*)
      CHARACTER NT*15
      COMMON /CCHR/ CPART,CC(75,2),C0(75),TC(75),ZC(75,2)
      COMMON /COUN/ IPR(60),NUM(60),SEC(60)
      COMMON /CONCI/ CLAG,COINI,DLC,FCV,XSF1,XXKV,XXKW
      COMMON /FRNT/ ISE,PF(2),PS(2),PT(2),PZ(2)
      COMMON /VAPO/ ABL,AKS,CN,CV(2),CVF(2),DAIR,XJV(2),ZV(2)
      COMMON /HIPR/ IHIST,NTIMES,PR(10),NZS,HI(5)
      COMMON /GAEQ/ CHS(2),DO,EE,FF,GA1,GA2,GA3,GA4,HS,IGA,IP,ZGA
      COMMON /MATR/ ETA,OMSOR,OMSWR,SR,SWR
      COMMON /NAME/ NT(15)
      COMMON /OCHR/ DLO,OLAG,SI(75,2),S0(75),T0(75),ZI(75,2)
      COMMON /OUTP/ ERCMX,EROMX,NPT,NREG
      COMMON /POLL/ DPA,DPL,DTP,DZPMDT,DZPDDT,IAT,PKS,PVOL,QP,SPMAX,SPR,
     1              THPZ,TPB,TPE,TPR,WP(50),XKPMX,XK22
      COMMON /RLTV/ KRF,XLAMB,EPS,EM1,EM2,CC1,REM1
      COMMON /WTER/ IRT,SWMAX,QW,WKS
      EXTERNAL SLOPE,PKE,WKE
      NUM(15) = NUM(15) + 1
C
      DO 1 I=1,51
        ZZ(I,2) = DPA
        ZZ(I,3) = DPA
 1    CONTINUE
      ZZ(1,1) = DPL
      DO 2 I=1,2
        PT(I) = TPB
        PZ(I) = DPL
        PS(I) = SPR
        PF(I) = 0.
 2    CONTINUE
C
C     ***WATER COMPUTATIONS
C     ***CONSTANT WATER SATURATION ABOVE THE WATERTABLE
C     ***ASSUMED REPRESENTATIVE OF CLIMATIC CONDITIONS
      CALL BISEC (WKE,0.5,1.,1.E-5,104,0,0.5,1.,SLIM,XXX,IE)
      SAR = 1.-SLIM
      IF (IRT.EQ.1) THEN
C       ***WATER FLUX SPECIFIED
        SWMAX = SWR
        IF (QW.GT.0.) SWMAX = SWR + OMSWR*((QW/WKS)**(1./EPS))
      ELSE
C       ***WATER SATURATION SPECIFIED
        IF (SWMAX.GT.1.-SAR) SWMAX = 1.-SAR
        CALL WKE (0,SWMAX,0,WKS,QW,0.,0)
      END IF
      WRITE (6,9500) SWMAX,QW
      IF (QW.GE.0.5*WKS) STOP 'START: WATER FILLS PORE SPACE'
C
C     ***PRELIMINARY OIL COMPUTATIONS
      NEQ(1) = 1
      IGA = 0
      IF (IAT.EQ.1.OR.IAT.EQ.3) THEN
        SPMAX = 1.-SWMAX-SAR
        CALL PKE (0,SPMAX,0,SWMAX,XKPMX,0.,0)
        CPART = COINI*QP/(QP + XXKW*QW)
      ELSE IF (IAT.EQ.2) THEN
        THPZ = DPL - DPA
        SPMAX = PVOL/ETA/THPZ
        IF (SPMAX.LT.SPR) WRITE (6,9505) THPZ,SPMAX
        IF (SPMAX.GT.1.-SWMAX-SAR) THEN
          SPMAX = 1.-SWMAX-SAR
          PVOL = SPMAX*ETA*THPZ
          WRITE (6,9510) SPMAX,PVOL
        END IF
        CALL PKE (0,SPMAX,0,SWMAX,QP,0.,0)
        XKPMX = QP
        Z = DPL
        DZ = THPZ*0.1
        DO 15 I=51,41,-1
          ZI(I,2) = Z
          ZI(I,1) = Z
          ZZ(I,2) = Z
          J = 51-I+1
          ZC(J,2) = Z
          ZC(J,1) = Z
          ZZ(J,3) = Z
          Z = Z - DZ
 15     CONTINUE
        CPART = PVOL*COINI/RD(SPMAX,SWMAX)/THPZ
      END IF
      IF (IP.EQ.0.AND.QP.GT.XKPMX) THEN
        QP = XKPMX
        PVOL = QP*DTP
        CPART = COINI*QP/(QP + XXKW*QW)
      END IF
      IF (QP.LE.0..AND.IAT.NE.3) THEN
        NEQ(1) = 0
        NEQ(2) = 0
      ELSE IF (QP.LE.XKPMX.AND.IAT.NE.3) THEN
C       ***KINEMATIC OIL FLOW
        SL = SPR
        IF (SL.GT.SPR) SL = QP/PKS
        TOL = 1.E-3
 45     CONTINUE
          CALL BISEC (PKE,SL,1.,TOL,110,1,QP,SWMAX,SPMAX,XX,IE)
          CALL PKE (0,SPMAX,0,SWMAX,XKPMX,0.,0)
C         ***ASSURE THAT SPMAX GIVES FLUX CLOSE TO LOADING RATE
          IF (ABS(XKPMX-QP).GT.5.E-5) THEN
            IF (TOL.LT.1.E-10) STOP 'OIL-TOLERANCE'
            TOL = TOL*0.1
            GO TO 45
          END IF
        DZPMDT = QP/ETA/SPMAX
      ELSE IF (IAT.EQ.3.OR.QP.GT.XKPMX) THEN
C       ***PRESSURIZED OIL FLOW
        EE = XKPMX*(1.-SPMAX*ETA)
        FF = XKPMX*QP
        ZZ(1,1) = DPA+0.001
        IGA = 1
C       C0(1) = COINI
        CHS(1) = 0.000001
        CHS(2) = 0.
        IF (IP.EQ.3) THEN
          GA1 = SPMAX*ETA/XKPMX
          GA2 = ALOG( HS )
          GA3 = HS - DPA
          GA4= DPA - (HS-DPA)*ALOG(HS)
          ZZ(1,1) = DPA
C         NEQ(1) = 0
```

```
        END IF
        DO = 0.
        IF (DLO.GT.0.) THEN
          DO = DLO
          DLO = 0.
        END IF
      END IF
      IF (IAT.EQ.1.AND.IGA.EQ.0.OR.(IGA.EQ.1.AND.IP.EQ.1)) THEN
        WRITE (6,9520) QP,PVOL
        IF (COINI.GT.0.) WRITE (6,9525) QP*DTP*COINI*FCV
      END IF
      CALL SLOPE (0,SPMAX,0,SWMAX,DZPDDT,0.,0)
      DZPDDT = DZPDDT/ETA
      ZGA = DPA + QP*DTP/SPMAX/ETA
      PS(1) = SPMAX
      NEQ(2) = 0
      IF (COINI.GT.0..AND.DLO.GT.0.) THEN
        CODM = XXKW*CPART*RD(SPMAX,SWMAX)/RD(0.,SWMAX)
        WRITE (6,9530) CODM
      END IF
C
C     ***STARTING VALUES FOR CHARACTERISTICS
      IL = 40
      IF (IAT.NE.2) IL = 51
      DO 4  J=1,2
        DO 3 I=1,IL
          ZI(I,J) = DPA
          ZC(I,J) = DPA
          SI(I,J) = SPMAX
          CC(I,J) = CPART
 3      CONTINUE
 4    CONTINUE
      DT = DTP*0.1
      T  = TPB - DT
      DO 20 I=51,41,-1
        T = T + DT
        T0(I) = T
        S0(I) = SPMAX
        J = 51-I+1
        TC(J) = T
        C0(J) = CPART
        NEQ(3) = J
 20   CONTINUE
      IF (COINI.EQ.0.) NEQ(3) = 0
      IF (COINI.GT.0..AND.IGA.EQ.1) THEN
        IF (IP.EQ.1) STOP 'FEATURE IP=1 NOT SUPPORTED FOR COINI.GT.0'
        C0(1) = COINI
        CC(1,2) = COINI
        CC(1,1) = COINI
C       ***ADD MORE CONSTITUENT CHARACTERISTICS FOR GREEN-AMPT CASES
        DO 40 I=NEQ(3),2,-1
          TC(I+4) = TC(I)
          C0(I+4) = C0(I)
 40     CONTINUE
        DT = DT/5.
        T = TC(1)
        DO 50 I=2,5
          T = T + DT
          TC(I) = T
          CO(I) = CPART
 50     CONTINUE
        NEQ(3) = NEQ(3) + 4
      END IF
      IF (XXKV.GT.0.) THEN
         CN = 10./3.
         IF (IAT.EQ.2) NEQ(1) = 2
         ZZ(2,1) = DPA
      END IF
      DS = (SPMAX-SPR)/40.
      SO = SPR - DS
      DO 65 I=1,40
        SO = SO + DS
        TO(I) = TPE
        SO(I) = SO
        SI(I,1) = SO
        SI(I,2) = SO
 65   CONTINUE
      CALL INQSET (SLOPE,SPR,1.-SWMAX,SWMAX,50,WP)
      IF (DLO.GT.0..AND.QP.GT.0.) NEQ(2) = 51
C
C     ***HEADINGS FOR OUTPUT FILES
      WRITE (6,9580) (NT(II),II=1,15)
      WRITE (6,9585)
      IF (IGA.EQ.1) THEN
        WRITE(6,9588)1,TPB,ZZ(1,1),CHS(2),SPMAX,PF(2),0.,ZC(1,2),ZV(2),
     1  CC(1,2)*XXKW,0.,0.
 9588   FORMAT (1X,I5,12F10.4)
      ELSE
        WRITE (6,9588)1,TPB,ZZ(1,1),0.,SPMAX,QP,0.,ZC(1,2),ZV(2),
     1  CC(1,2)*XXKW,0.,0.
      END IF
      WRITE (10,9100) (NT(I),I=1,15),(HI(I),I=1,NZS)
      IF (NZS.EQ.1) WRITE (10,9102)
      IF (NZS.EQ.2) WRITE (10,9103)
      IF (NZS.EQ.3) WRITE (10,9104)
 9500 FORMAT (15X,30HWATER SATURATION            = ,F10.4/
     1        15X,30HWATER FLUX                  = ,F10.4)
 9505 FORMAT (15X,30HTHICKNESS OF POLLUTED ZONE  = ,F10.4/
     2        15X,30HMAXIMUM OIL SATURATION      = ,F10.4)
 9510 FORMAT (15X,34HOIL SAT. REDUCED TO MAX. ALLOWABLE/
     1        15X,30HADJUSTED OIL SATURATION     = ,F10.4/
     2        15X,30HADJUSTED OIL VOLUME/AREA    = ,F10.4)
 9520 FORMAT (15X,30HPOLLUANT VOLUME FLUX        = ,F10.4/
     1        15X,30HTOTAL OIL LOADING, VOL/AREA = ,F10.4)
 9525 FORMAT (15X,30HTOTAL CONSTITUENT LOADING   = ,F10.4)
 9530 FORMAT (15X,30HMAX. CONC. DUE TO OIL DECAY = ,F10.4)
 9580 FORMAT (1H1//28X,50(1H*)/
     1        33X,'LOCATION OF THE OIL AND CONSTITUENT FRONTS'/
     2        28X,50(1H*)/
     4        3(28X,5A10/)/)
 9585 FORMAT (/
     1        16X,23X,'OIL',24X,30X,'CONSTITUENT'/
     2        18X,48(1H-),1X,49(1H-)/
     2        1X,' STEP',4X,'TIME',2X,3X,'DEPTH',2X,4X,'HEAD',2X,
     3           'SATURATION',4X,'FLUX',2X,1X,'VOL/AREA',1X,9X,'DEPTHS'
     4           ,5X,5X,'CONC',1X,1X,'MASS/AREA',1X,'CUMULATIVE'/
     5        26X,10X,30X,4X,'LOWER',1X,4X,'UPPER',20X,'VOLATILIZATION'/
     6        1X,115(1H=)/)
 9100 FORMAT (//10X,50(1H*)/
     1        10X,'      SATURATION AND CONCENTRATION HISTORIES'/
     2        10X,50(1H*)/
     3        3(10X,5A10/)/
     4        1X,10H   TIME   ,12X,'DEPTH(S)'/
     5        10X,3(10X,F10.4,10X))
 9102 FORMAT (10X,(4X,'SAT',3X,4X,'FLUX',2X,3X,'CONC',3X)/
     1        1X,9(1H=),(1X,29(1H=)))
 9103 FORMAT (10X,2(4X,'SAT',3X,4X,'FLUX',2X,3X,'CONC',3X)/
     1        1X,9(1H=),2(1X,29(1H=)))
 9104 FORMAT (10X,3(4X,'SAT',3X,4X,'FLUX',2X,3X,'CONC',3X)/
     1        1X,9(1H=),3(1X,29(1H=)))
      RETURN
      END
      SUBROUTINE COUNT
      CHARACTER NT*15
      COMMON /COUN/ IPR(60),NUM(60),SEC(60)
      COMMON /FRNT/ ISE,PF(2),PS(2),PT(2),PZ(2)
      COMMON /NAME/ NT(15)
      COMMON /OUTP/ ERCMX,EROMX,NPT,NREG
      CHARACTER CN(60)*6
C---*-+-+$+-+-*-+-+$----*----$----*----$----*----$----*----$----*----$--
XX*XXXX
      DATA (CN(I),I=1,29) /'MAIN','PFRONT','PCHK','GACHK','GAHS',
     1     'RD','CVEL','CONC','OCP','ZMASS','OIL','HIST',
     2     'SFLUX','INPUT','START','COUNT','MRKF12','GLQ','INQUAD',
     3     'BINARY','BISEC','WKE',' ','PKE','SLOPE',' ','KRSET',
     4     'INQSET',' '/
C
      NUM(16) = NUM(16) + 1
C     ***RUN INFORMATION
      WRITE (6,9500) (NT(II),II=1,15)
      WRITE (6,9501)
      N1 = 0
      NEND = 28
 90   CONTINUE
        IF (N1.GT.NEND) GO TO 100
        N1 = N1 + 1
        IF (CN(N1).EQ.' ') GO TO 90
        N2 = N1 + 1
 95     CONTINUE
        IF (CN(N2).EQ.' '.AND.N2.NE.NEND) THEN
          N2 = N2 + 1
          GO TO 95
        END IF
        IF (CN(N2).NE.' ') THEN
          WRITE (6,9503) N1,CN(N1),NUM(N1),N2,CN(N2),NUM(N2)
        ELSE
          WRITE (6,9503) N1,CN(N1),NUM(N1)
        END IF
        N1 = N2
        GO TO 90
 100  CONTINUE
      X1 = FLOAT(NUM(2))
      X2 = FLOAT(NPT+NREG)
      X3 = FLOAT(NPT)
      WRITE (6,9820) NPT+NREG,NPT,NREG,NUM(2),X1/X2,X1/X3,FLOAT(ISE)/X1
      WRITE (6,9900)
      STOP 'END'
C
C     ***OUTPUT FORMATS
 9500 FORMAT (1H1//10X,40HUNSTEADY IMMISCIBLE GROUNDWATER POLLUTAN,
     1              14HT INFILTRATION/
     2         10X,20X,15HRUN INFORMATION/
     3         10X,54(1H*)/
     4         3(12X,5A10/)/)
 9501 FORMAT (10X,20HROUTINE        CALLS,14X,20HROUTINE        CALLS/
     1         10X,20(1H=),14X,20(1H=)/)
 9503 FORMAT (8X,I4,3X,A6,3X,I6,12X,I4,3X,A6,3X,I6)
 9820 FORMAT (//15X,'RUNGE-KUTTA-FEHLBERG SOLVER PERFORMANCE'/
     1         10X,54(1H=)//
     2         10X,'NUMBER OF TIME STEPS TAKEN                ',I10/
     3         10X,'ACCEPTED STEPS                            ',I10/
     4         10X,'REJECTED STEPS                            ',I10/
     5         10X,'FUNCTION EVALUATIONS                      ',I10/
     6         10X,'AVERAGE NO. EVALUATIONS PER STEP          ',F10.4/
     7         10X,'AVERAGE NO. EVALUATIONS PER ACCEPTED STEP ',F10.4/
     8         10X,'AVERAGE NO. EQUATIONS SOLVED PER EVAL.    ',F10.4/)
 9900 FORMAT (10X,'HISTORIES ARE IN DEFAULT FILE HIST'/
     1         10X,'PROFILES  ARE IN DEFAULT FILE PROF'/
     2         //10X,50(1H*)/
     3         10X,'SUCESSFUL EXECUTION'/
     4         10X,50(1H*))
      END
      SUBROUTINE WKE (IS,SW,N,XKS,XKR,SV,IE)
      COMMON /COUN/ IPR(60),NUM(60),SEC(60)
      COMMON /MATR/ ETA,OMSOR,OMSWR,SR,SWR
      COMMON /POLL/ DPA,DPL,DTP,DZPMDT,DZPDDT,IAT,PKS,PVOL,QP,SPMAX,SPR,
     1              THPZ,TPB,TPE,TPR,WP(50),XKPMX,XK22
      COMMON /RLTV/ KRF,XLAMB,EPS,EM1,EM2,CC1,REM1
C
C     ***RELATIVE PERMEABILITY VIA THE BROOKS-COREY INTEGRATION
C     ***OF THE WYLLIE AND GARDNER BURDINE EQUTIONS
      NUM(22) = NUM(22) + 1
      XKR = 0.
      IF (SW.LE.SWR) RETURN
      XKR = XKS*((SW - SWR)/OMSWR)**EPS
      RETURN
C
      ENTRY SWKE (IS,SW,N,XKS,SKR,SV,IE)
C     ***DERIVATIVE OF THE RELATIVE PERMEABILITY W.R.T. SW
      NUM(23) = NUM(23) + 1
      SKR = 0.
      IF (SW.LE.SWR) RETURN
      SKR = EPS*XKS*((SW - SWR)**EM1)*CC1
      RETURN
C
      ENTRY PKE (IS,SP,N,SW,PK,SVOL,IEND)
C     ***RELATIVE PERMEABILITY FOR OIL
      SPF = (SP - SPR)/OMSOR
      IF (SPF.LT.0.) SPF = 0.
      T1 = (SP + SW - SWR)/OMSWR
      IF (T1.GT.0.) T1 = T1**EM2
      T2 = (SW - SWR)/OMSWR
      IF (T2.GE.0.) T2 = T2**EM2
      PK = PKS*SPF*SPF*(T1 - T2)
      NUM(24) = NUM(24) + 1
      RETURN
C
      ENTRY SLOPE (IS,SP,N,SW,DKDSP,SVOL,IEND)
C     ***DERIVATIVE OF KR (OIL) WRT SP
      T3 = 0.
      EM3 = EM2 - 1.
      SPF = (SP - SPR)/OMSOR
      IF (SPF.LT.0.) SPF = 0.
      T1 = (SP + SW - SWR)/OMSWR
      IF (T1.GE.0.)  THEN
        T3 = T1**EM3
        T1 = T1**EM2
      END IF
      T2 = (SW - SWR)/OMSWR
      IF (T2.GE.0.)  T2 = T2**EM2
      DKDSP = 2.*SPF*(T1-T2)/OMSOR + EM2*SPF*SPF*T3/OMSWR
      DKDSP = DKDSP*PKS
      NUM(25) = NUM(25) + 1
      RETURN
C
      ENTRY KRSET
C     ***SET UP ROUTINE
      NUM(27) = NUM(27) + 1
      EPS = (2. + 3.*XLAMB)/XLAMB
      EM1 = EPS - 1.
      EM2 = EPS - 2.
      EM3 = EPS - 3.
      CC1 = 1./(OMSWR**EPS)
      REM1 = 1./EM1
      RETURN
      END
      SUBROUTINE MRKF12 (FNC,CHK,TX,TF,DM,ER,NEQ,NS,NR,YY,ND,ET)
C     **************************************************************
C     *                                                            *
C     *   MRKF12  (MULTIPLE) RUNGE KUTTA FELHBERG FIRST-SECOND     *
C     *           ORDER ORDINARY DIFFERENTIAL EQUATION SOLVER      *
C     *                                                            *
C     *                                                            *
C     *   PURPOSE....THIS SUBROUTINE SOLVES A SYSTEM OF ORDINARY   *
C     *   DIFFERENTIAL EQUATIONS OF THE FORM                       *
C     *                                                            *
C     *   DY/DT = F(Y,T)                                           *
C     *                                                            *
C     *   THE FUNCTIONS F(Z,T) ARE CONTAINED IN THE ROUTINE FNC.   *
C     *   THE EQUATIONS ARE IN 3 GROUPS, SOME OF WHICH MAY NOT BE  *
C     *   SOLVED AT ALL TIMES DURING THE SOLUTION PROCESS.         *
C     *   ROUTINE CHK CONTAINS CHECKS ON THE SOLUTION AND SWITCHES *
C     *   TO CONTROL THE EXECUTION.  THE FELHBERG FEATURE ALLOWS   *
C     *   THE TIME STEP TO VARY.                                   *
C     *                                                            *
C     *   INPUT ARGUMENTS.......................................   *
C     *   FNC   = SUBROUTINE WHICH CONTAINS FUNCTIONS F(Y,T)       *
C     *   CHK   = SUBROUTINE WHICH CONTAINS CHECKS AND CONTROLS    *
C     *   TX    = STARTING TIME                                    *
C     *   TF    = ENDING TIME                                      *
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C     *   DM    = MAXIMUM TIME STEP                                       *
C     *   ER    = ERROR TOLERANCE PER STEP                                *
C     *   NEQ   = ARRAY CONTAINING NUMBER OF EQUATIONS PER GROUP          *
C     *   NS    = STEP NUMBER (STARTING)                                  *
C     *   YY    = INITIAL CONDITION                                       *
C     *   ND    = ROW DIMENSION OF YY                                     *
C     *                                                                   *
C     *   OUTPUT ARGUMENTS.........................................      *
C     *   DM    = MAXIMUM TIME STEP                                       *
C     *   NEQ   = NUMBER OF EQUATIONS PER GROUP                           *
C     *   NS    = STEP NUMBER (ENDING)                                    *
C     *   NR    = NUMBER OF REJECTED STEPS                                *
C     *   YY    = SOLUTION AT ENDING TIME                                 *
C     *   ET    = ENDING TIME OF SOLUTION                                 *
C     *                                                                   *
C     *                                                                   *
C     *   AUTHOR  JIM WEAVER                                              *
C     *           THE UNIVERSITY OF TEXAS AT AUSTIN                       *
C     *                                                                   *
C     *   REFERENCE:  FEHLBERG, 1969, NASA TR R-315                       *
C     *   SINGLE PRECISION, ANSI STD. X3.9-1978 FORTRAN 77                *
C     *   REQUIRED ROUTINES...SEE INPUT ARGUMENTS                         *
C     *   X-21-87                                                         *
C     *                                                                   *
C     *********************************************************************
      COMMON /COUN/ IPR(60),NUM(60),SEC(60)
C     ***CAUTION: THE FIRST DIMENSION OF XK0,XK1,XK2 & YI MUST MATCH ND
      DIMENSION DTR(20),IRR(20),NEQ(*),XK0(55,3),XK1(55,3),XK2(55,3),
     1YI(55,3),YY(ND,*)
      PARAMETER (A1=0.5,B10=A1,B20=1./256.,B21=255./256.,C3=1./512.)
      DATA IRR,NDT /20*0,13/
      NUM(17) = NUM(17) + 1
      IF (ND.NE.55) STOP 'RUNGE-KUTTA'
C
C     ***INITIAL VALUES
      IC   = 0
      N    = NN
      DT   = 0.0001
      TN   = TX
      IU   = 0
C
 1    CONTINUE
C     ***SAVE INITIAL CONDITION IN CASE PROPOSED TIME STEP IS
C     ***TOO LARGE
      DO 25  J=1,3
        DO 20  I=1,NEQ(J)
          YI(I,J) = YY(I,J)
 20     CONTINUE
 25   CONTINUE
 30   CONTINUE
      DO 35 I=1,NDT
        DTR(I) = 1.E20
 35   CONTINUE
C     ***INTEGRATE ONE STEP
C     ***SET SOME CONSTANTS FOR THIS TIME STEP
      A1D  = DT * A1
      B10D = DT * B10
      B20D = DT * B20
      B21D = DT * B21
      C3D  = DT * C3
      XT = TN
C
C     ***BEGIN SERIES OF FUNCTION EVALUATIONS FOR CERTAIN
C     ***VALUES OF TN AND YY
      IF (IU.EQ.0) CALL FNC (XT,YI,XK0,ND,NEQ)
C
C     ***THE SECOND EVALUATION
      TN = XT + A1D
      DO 45  J=1,3
        DO 40  I=1,NEQ(J)
          IF (XK0(I,J).EQ.0.) GO TO 40
          YY(I,J) = YI(I,J) + B10D*XK0(I,J)
 40     CONTINUE
 45   CONTINUE
      CALL FNC (TN,YY,XK1,ND,NEQ)
C
C     ***THE THIRD EVALUATION
      TN = XT + DT
      DO 55  J=1,3
        DO 50  I=1,NEQ(J)
          YY(I,J) = YI(I,J) + B20D*XK0(I,J) + B21D*XK1(I,J)
 50     CONTINUE
 55   CONTINUE
      CALL FNC (TN,YY,XK2,ND,NEQ)
C
C     ***DETERMINE NEW TIME STEP FROM THE FUNCTION EVALUATIONS
      IE = 0
      IE2 = 0
      TR = 1000.
      DO 75  J=1,3
        DO 70  I=1,NEQ(J)
          IF (XK0(I,J).EQ.XK2(I,J)) GO TO 70
          IF (XK0(I,J).EQ.0..AND.XK2(I,J).GT.0.) GO TO 70
          TE = ABS(  C3D*(XK0(I,J) - XK2(I,J))  )
          BB = TE / (AMAX1 (1., ABS(  YY(I,J)     ) ) )
          IF (BB.GT.ER) THEN
C           ***STEP REJECTED
            IE = 1
            DTR(1) = DT*.5
            GO TO 76
          END IF
          TS = DT * (   (ER + ER*ABS(YY(I,J)    ) )/TE  ) ** 0.25
          IF (TS.LT.TR) TR = TS
 70     CONTINUE
 75   CONTINUE
 76   CONTINUE
      IE2 = 0
      DT1 = DT
      CALL CHK (TN,YY,YI,ND,NEQ,DM,DT1,DTR,NS,IC,IRR,IE2,IE)
      ET = TN
      IF (IC.EQ.1) RETURN
      IF (IE2.EQ.1) IU = 0
      IF (IE.EQ.1.OR.IE2.EQ.1) THEN
C       ***REJECT STEP
        NR = NR + 1
        TN = XT
```

```
C        ***SELECT SMALLEST STEP SIZE LIMITATION
         DT = 1.E19
         DO 80 II=1,NDT
           IF (DTR(II).LT.DT.AND.DTR(II).GT.0.) THEN
             DT = DTR(II)
             IN = II
           END IF
 80      CONTINUE
         IRR(IN) = 1
         IF (DT.GE.1.E19) STOP 'RKF: DT=1.E19'
         GO TO 30
       END IF
       NS = NS + 1
C      ***SET NEW TIME STEP
       IU = 1
       IF (DT1.LT.DT) TR = DT1*1.25
       DT = TR * 0.80
       IF (DT.GT.DM) DT = DM
C      ***THIRD EVALUATION BECOMES FIRST EVALUATION
       DO 95 J=1,3
         DO 90 I=1,NEQ(J)
           XK0(I,J) = XK2(I,J)
 90      CONTINUE
 95    CONTINUE
       GO TO 1
       END
       SUBROUTINE GLQ (FNC,A1,NEQ,A,B,IW,SUM)
C     ****************************************************************
C     *                                                              *
C     *   GLQ    SEVEN POINT GAUSS LAGRANGE QUADRATURE               *
C     *                                                              *
C     *                                                              *
C     *   PURPOSE....THIS SUBROUTINE EVALUATES INTEGRALS BY SEVEN    *
C     *   POINT GAUSS-LAGRANGE QUADRATURE                            *
C     *                                                              *
C     *   INPUT ARGUMENTS.......................................     *
C     *   FNC    = NAME OF ROUTINE CONTAINING INTEGRAND              *
C     *   A1     = PARAMETER PASSED TO FNC                           *
C     *   NEQ    = ARRAY CONTAINING NUMBER OF EQUATIONS              *
C     *   A      = LOWER LIMIT OF INTEGRATION                        *
C     *   B      = UPPER LIMIT OF INTEGRATION                        *
C     *   IW     = WRITE PARARMTER IW=1 WRITE INTO FILE 10           *
C     *                                                              *
C     *   OUTPUT ARGUMENTS......................................     *
C     *   SUM    = VALUE OF INTEGRAL                                 *
C     *                                                              *
C     *   AUTHOR  JIM WEAVER                                         *
C     *           THE UNIVERSITY OF TEXAS AT AUSTIN                  *
C     *                                                              *
C     *   REFERENCES: ABRAMOWITZ AND STEGUN, P. 916                  *
C     *   SINGLE PRECISION, ANSI STD. X3.9-1978 FORTRAN 77           *
C     *   REQUIRED ROUTINES...SEE INPUT ARGUMENTS                    *
C     *   II-17-87                                                   *
C     *                                                              *
C     ****************************************************************
       REAL CS(7),CY(7)
       COMMON /COUN/ IPR(60),NUM(60),SEC(60)
       DATA CY /-.949108,-.741531,-.405845,0.,.405845,.741531,.949108/
```

```
      DATA CS /.129485,.279705,.381830,.417959,.381830,.279705,.129485/
      NUM(18) = NUM(18) + 1
      C1 = (B - A)*0.5
      C2 = (B + A)*0.5
C
C     ***FUNCTION EVALUATIONS AT GAUSS POINTS
      SUM = 0.
      DO 10 I=1,7
        Y = CY(I)*C1 + C2
        CALL FNC (Y,A1,A2,NEQ,VAL)
        IF (IW.EQ.1) WRITE (9,9101) Y,VAL
        SUM = SUM + VAL*CS(I)
 10   CONTINUE
      SUM = SUM*C1
 9101 FORMAT (15X,F10.4,5X,F10.4)
      RETURN
      END
      SUBROUTINE INQUAD (X,NX,AMIN,AMAX,VA,RE)
C     ***************************************************************
C     *                                                             *
C     *   INQUAD                                                    *
C     *                                                             *
C     *                                                             *
C     *   PURPOSE....THIS SUBROUTINE PERFORMS INVERSE QUADRATIC     *
C     *   INTERPOLATION ON A SET OF PREDETERMINED NUMBERS TO        *
C     *   INVERT A NONLINEAR FUNCTION.  INQSET IS CALLED FIRST      *
C     *   TO SET UP THE ARRAY OF FUNCTION VALUES.  SUBSEQUENT       *
C     *   CALLS TO INQUAD GIVE THE INVERSE FOR SPECIFIED VALUES     *
C     *   OF THE DEPENDENT VARIABLE                                 *
C     *                                                             *
C     *   INPUT ARGUMENTS.........................................  *
C     *   X      = ARRAY OF FUNCTION VALUES FROM INQSET             *
C     *   NX     = NO. OF X'S                                       *
C     *   AMIN   = MINIMUM INDEPENDENT VARIABLE VALUE               *
C     *   AMAX   = MAXIMUM INDEPENDENT VARIABLE VALUE               *
C     *   VA     = VALUE OF DEPENDENT VARIABLE                      *
C     *                                                             *
C     *   OUTPUT ARGUMENTS........................................  *
C     *   RE     = VALUE OF INDEPENDENT VARIABLE:  VA = F(RE)       *
C     *                                                             *
C     *                                                             *
C     *   AUTHOR  JIM WEAVER                                        *
C     *           THE UNIVERSITY OF TEXAS AT AUSTIN                 *
C     *                                                             *
C     *   REFERENCES: ABRAMOWITZ AND STEGUN, PG. 882.               *
C     *   SINGLE PRECISION, ANSI STD. X3.9-1978 FORTRAN 77          *
C     *   REQUIRED ROUTINES...INQSET                                *
C     *                                                             *
C     *                                                             *
C     ***************************************************************
      COMMON /COUN/ IPR(60),NUM(60),SEC(60)
      REAL X(*)
      DATA I /1/
      NUM(19) = NUM(19) + 1
      DX = (AMAX - AMIN)/FLOAT(  NX - 1  )
      CALL BINARY (VA,X,NX,1,I)
      IF (I.EQ.1.OR.I.EQ.NX-1) THEN
        P = (VA - X(I))/(X(I+1) - X(I))
      ELSE IF (I.LT.NX) THEN
        A = X(I+1) - 2.*X(I) + X(I-1)
        B = X(I+1) - X(I-1)
        C = 2.*(X(I) - VA)
        Q = B*B - 4.*A*C
        IF (Q.LT.0.) STOP 240
        Q = SQRT(  Q  )
        P = (Q - B)*0.5/A
      ELSE
        WRITE (7,1010) I,NX,AMIN,AMAX,VA,X(1),X(NX)
 1010   FORMAT (1X,'INQUAD: I,NX,MIN,MAX,VA,X(1),X(NX)',2I5,5F10.4)
        STOP 241
      END IF
      RE = AMIN + (FLOAT(I-1) + P)*DX
      RETURN
C
      ENTRY INQSET (FNC,AMIN,AMAX,PARA,NX,X)
C     ***************************************************************
C     *                                                             *
C     *   PURPOSE....THIS SUBROUTINE SETS UP ARRAYS FOR INQUAD      *
C     *                                                             *
C     *   INPUT ARGUMENTS.......................................    *
C     *   FNC    = SUBROUTINE NAME OF A NONLINEAR FUNCTION          *
C     *   AMIN   = MINIMUM VALUE OF INDEPENDENT VARIABLE            *
C     *   AMAX   = MAXIMUM VALUE OF INDEPENDENT VARIABLE            *
C     *   PARA   = REAL PARAMETER PASSED TO FNC                     *
C     *   NX     = NUMBER OF DEPENDENT VALUES TO PRODUCE            *
C     *                                                             *
C     *   OUTPUT ARGUMENTS......................................    *
C     *   X      = ARRAY OF DEPENDENT VARIABLES                     *
C     *                                                             *
C     ***************************************************************
      NUM(28) = NUM(28) + 1
      SS = AMIN
      DX = (AMAX - AMIN)/FLOAT(  NX - 1  )
      DO 1  I=1,NX
        CALL FNC (0,SS,0,PARA,X(I),0.,0)
        SS = SS + DX
 1    CONTINUE
      RETURN
      END
      SUBROUTINE BINARY (U,X,NX,INCX,IN)
C     ***************************************************************
C     *                                                             *
C     *   BINARY                                                    *
C     *                                                             *
C     *                                                             *
C     *   PURPOSE....THIS SUBROUTINE PERFORMS A BINARY SEARCH ON    *
C     *   THE ARRAY X TO FIND THE INDEX OF THE X VALUE WHICH LIES   *
C     *   JUST BELOW U                                              *
C     *                                                             *
C     *   INPUT ARGUMENTS.......................................    *
C     *   U      = POINT SEARCHED FOR                               *
C     *   X      = ARRAY OF VALUES                                  *
C     *   NX     = NUMBER OF X VALUES                               *
C     *   INCX   = INCREMENT (MUST = 1)                             *
C     *                                                             *
C     *   OUTPUT ARGUMENTS......................................    *
```

```
C     *   IN     = INDEX OF X VALUE JUST BELOW U                    *
C     *                                                             *
C     *                                                             *
C     *   AUTHOR  JIM WEAVER                                        *
C     *           THE UNIVERSITY OF TEXAS AT AUSTIN                 *
C     *                                                             *
C     *   REFERENCE:  FORSYTHE, MALCOLM AND MOLER, 1977, PG. 76     *
C     *   SINGLE PRECISION, ANSI STD. X3.9-1978 FORTRAN 77          *
C     *   REQUIRED ROUTINES...NONE                                  *
C     *                                                             *
C     ***************************************************************
      COMMON /COUN/ IPR(60),NUM(60),SEC(60)
      REAL X(*)
      DATA I/1/
C
      NUM(20) = NUM(20) + 1
      IF (INCX.NE.1) STOP 'BINARY-INDEX'
C     ***X'S ORDERED BY INCREASING VALUE
      IF (X(1).LT.X(NX)) THEN
        IF (I.GT.NX) I = 1
        IF (U.LT.X(I).OR.X(I+1).LT.U) THEN
          IF (U.LT.X(I)) THEN
            J = I
            I = 1
          ELSE
            I = I + 1
            J = NX
          END IF
 2        CONTINUE
            K = (I + J)/2
            IF (U.LT.X(K)) J = K
            IF (U.GE.X(K)) I = K
          IF (J.GT.I+1) GO TO 2
        END IF
        IN = I
        IF (IN.EQ.NX) IN = IN - 1
      ELSE IF (X(1).GT.X(NX)) THEN
C       ***X'S ORDERED BY DECREASING VALUES
        IF (I.GT.NX) I = 1
        IF (U.LT.X(I+1).OR.X(I).LT.U) THEN
          IF (U.LT.X(I+1)) THEN
            J = NX
            I = I + 1
          ELSE
            J = I
            I = 1
          END IF
 5        CONTINUE
            K = (I + J)/2
            IF (U.LT.X(K)) I = K
            IF (U.GE.X(K)) J = K
          IF (J.GT.I+1) GO TO 5
        END IF
        IN = I
      END IF
      RETURN
      END
      SUBROUTINE BISEC (FNC,ZB,ZE,CONV,IS,NN,SV,TM,ZM,VM,IE)
```

```
C     **************************************************************
C     *                                                            *
C     *   BISEC                                                    *
C     *                                                            *
C     *                                                            *
C     *   PURPOSE....THIS SUBROUTINE USES THE BISECTION METHOD TO  *
C     *   FIND THE ZERO OF A FUNCTION                              *
C     *                                                            *
C     *   INPUT ARGUMENTS.......................................   *
C     *   FNC    = SUBROUTINE NAME CONTAINING FUNCTION             *
C     *   ZB     = LOWER LIMIT OF SEARCH                           *
C     *   ZE     = UPPER LIMIT OF SEARCH                           *
C     *   CONV   = CONVERGENCE TOLERANCE                           *
C     *   IS     = MAXIMUM NUMBER OF ITERATIONS                    *
C     *   NN     = 1NTEGER PASSED TO FNC                           *
C     *   SV     = FUNCTION VALUE TO BE MATCHED BY BISEC ITERATION *
C     *   TM     = REAL NUMBER PASSED TO FNC                       *
C     *                                                            *
C     *   OUTPUT ARGUMENTS......................................   *
C     *   ZM     = BISEC RESULT (ZB.LE.ZM.LE.ZE)                   *
C     *   VM     = FUNCTION VALUE AT ZM (SHOULD MATCH SV)          *
C     *   IE     = ERROR CODE IE=-1: BISEC FAILED                  *
C     *                                                            *
C     *                                                            *
C     *   AUTHOR  JIM WEAVER                                       *
C     *           THE UNIVERSITY OF TEXAS AT AUSTIN                *
C     *                                                            *
C     *   REFERENCE: FORSYTHE, MALCOLM & MOLER, 1977, PG. 157      *
C     *   SINGLE PRECISION, ANSI STD. X3.9-1978 FORTRAN 77         *
C     *   REQUIRED ROUTINES...SEE INPUT ARGUMENTS                  *
C     *   THANKS TO SHERYL FRANKLIN                                *
C     **************************************************************
C
      COMMON /COUN/ IPR(60),NUM(60),SEC(60)
      NUM(21) = NUM(21) + 1
      T1 = 1.
      T2 = 1.
      XF = 1.
      Z0 = ZB
      ZF = ZE
      CALL FNC (IS,Z0,NN,TM,V1,SV,IE)
      IF (V1.GT.SV) XF = -1.
      Z1 = V1 - SV
      SVV = SV
      CALL FNC (IS,ZF,NN,TM,V2,SV,IE)
      IF (SIGN(T1,Z1).EQ.SIGN(T2,V2-SV)) THEN
        IE = -1
        WRITE (7,7020) IS,SIGN(T1,V1-SV),SIGN(T2,V2-SV)
        WRITE (7,7025) T1,V1,SVV,T2,V2,SV
 7025   FORMAT (1X,'BISEC: T1,V1,SVV,T2,V2,SV',6G10.4)
 7020   FORMAT (1X,'BISEC: IS,SIGNS',I5,2F10.4)
        RETURN
      END IF
      DO 1  I=1,IS
        ZM = Z0 + (ZF - Z0)*0.5
        CALL FNC (IS,ZM,NN,TM,VM,SV,IE)
        XM = XF*(VM - SV)
        IF (ABS(XM).LE.CONV) RETURN
        IF (XM.GE.0.) THEN
        ZF = ZM
       ELSE
        Z0 = ZM
       END IF
  1   CONTINUE
      STOP 'BISEC: FAIL'
      END
```